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(54) **New hydrazine derivative and pesticidal composition comprising said derivative as an effective ingredient**

Hydrazinderivat und dieses Derivat als wirksamen Bestandteil enthaltende pestizide Zusammensetzung

Dérivé d'hydrazine et composition pesticide contenant ce dérivé comme ingrédient actif

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(56) References cited:
EP-A- 0 228 564 **EP-A- 0 286 746**

- **PATENT ABSTRACTS OF JAPAN vol. 15, no. 357 (C-866)10 September 1991**
- **English translation of JP-A-3141245**

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Description

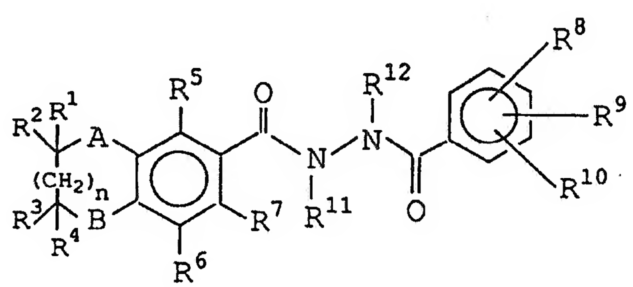
The present invention relates to a novel hydrazine derivative which can be utilized as a pesticide in paddy field, upland field, orchard, forest or places to be kept environmentally hygiene and as a parasiticide for protecting human being or animals from injury of a parasite.

In Japanese Patent Application Laid-Open (KOKAI) No. 62-167747(1987) (USP 4,985,461, EP 236618), No. 62-263150(1987) and No. 3-141245 (1991), there are described that N-substituted-N'-substituted-N,N'-diacylhydrazine derivative has pesticidal activity. EP-A-0 286 746 discloses N-(optionally substituted)- N'-substituted-N-N'-disubstituted hydrazines which have inserticidal activity. EP-A-0 228 564 discloses unsubstituted and substituted diacylhydrazine compounds useful as insecticidal agents. However, in these patent publications, the derivative of the present invention mentioned below has never been described.

For controlling harmful pest in paddy field, upland field, orchard, forest or places to be kept environmentally hygienic, there have been demanded a compound having a higher pesticidal activity without damaging useful insects, circumstance, etc. and having a low toxicity to human and animal. Also, in recent years, the number of harmful pest which shows resistance to known pesticides such as an organophosphorus compound, a carbamate compound, a pyrethroid, etc. is increasing and control thereof becomes difficult whereby a new type pesticidal compound is now demanded.

The present invention is to provide a new type pesticidal compound which substantially does not affect to useful insects, environment, etc., has a low toxicity to human and animal and shows an excellent control effect against chemical-resistant harmful pests, and a pesticidal composition containing the compound as an effective ingredient.

The pesticidal compound of the present invention is represented by the following formula (I):



(I)

wherein

A, B, R^1, R^2, R^3 and R^4, R^5, R^6 and R^7 R^8, R^9, and R^{10}, R^{11}, R^{12} and n are defined as in claim 1.

In the formula (I),

the halogen atom may include fluorine atom, chlorine atom, bromine atom and iodine atom;

the (C_1-C_4)alkyl group may include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl,sec-butyl and t-butyl group;

the (C_2-C_4)alkenyl group may include allyl, 2-propenyl, 1-propenyl, ethenyl and 2-butenyl group;

the (C_1-C_4)alkoxy group may include methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, isobutoxy and t-butoxy group;

the hydroxy(C_1-C_4)alkyl group may include 2-hydroxyethyl and hydroxymethyl group;

the (C_1-C_4)alkoxy(C_1-C_4)alkoxy group may include ethoxymethoxy, methoxyethoxy, ethoxyethoxy, n-propoxymethoxy, isopropoxymethoxy and n-butoxymethoxy group;

the (C_2-C_4)alkynyl group may include ethynyl, propynyl and butynyl group;

the (C_1-C_4)haloalkyl group may include 1- or 2-chloroethyl, chloromethyl, dichloromethyl, bromomethyl, 1- or 2-bromoethyl, fluoromethyl, difluoromethyl and trifluoromethyl group;

the (C_1-C_4)haloalkoxy group may include 1- or 2-bromoethoxy, 3-bromo-n-propoxy, 2,2,2- or 1,1,2-trifluoroethoxy and trifluoromethoxy group;

the (C_2-C_4)alkynyloxy group may include allyloxy and 2-butenyloxy group;

the (C_2-C_4)alkynyloxy group may include propargyloxy and butynyloxy group;

the (C_1-C_4)alkoxy group having a phenyl group which is optional substituted by a halogen atom may include 2-(p-chlorophenyl)ethoxy, m-chlorophenylmethoxy, 2-(p-fluorophenyl)ethoxy, 2-(m-fluorophenyl)ethoxy and 3-(p-bromophenyl)propoxy group;

the (C_1-C_4)alkylthio(C_1-C_4)alkyl group may include methylthiomethyl, 2-methylthioethyl, 3-isopropylthiopropyl, n-

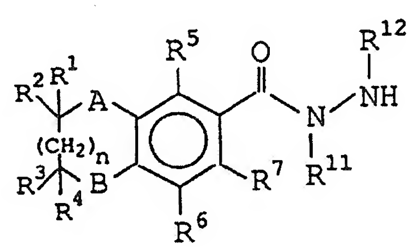
butylthiomethyl and 2-ethylthioethyl group;
the tri(C_1-C_4)alkylsilyloxy(C_1-C_4)alkyl group may include trimethylsilyloxymethyl, trimethylsilyloxyethyl and dimethyl-t-butylsilyloxymethyl group;
the (C_1-C_4)alkoxy group having a phenoxy group which is optionally substituted by a CF_3, halogen atom or (C_1-C_2)alkyl group may include 2-(m-trifluoromethylphenoxy)ethoxy, 3-phenoxypropoxy, 2-(m-methylphenoxy)ethoxy, 2-(p-chlorophenoxy)ethoxy and 2-(p-fluorophenoxy)ethoxy group;
the (C_1-C_4)haloalkylthio group may include 2-chloroethylthio, 2-bromoethylthio, trichloromethylthio, fluorodichloromethylthio, trifluoromethylthio and 2-fluoropropylthio group;
the (C_2-C_5)acyl group may include acetyl and propionyl group;
the (C_1-C_4)alkoxycarbonylcarbonyl group may include t-butoxycarbonylcarbonyl, methoxycarbonylcarbonyl and ethoxycarbonylcarbonyl group;
the (C_1-C_4)alkoxycarbonyl group may include ethoxycarbonyl, methoxycarbonyl, isopropoxycarbonyl and isobutoxycarbonyl group;
the (C_1-C_4)alkyl group which is optionally substituted by a (C_1-C_6)alkylcarbonyloxy group or (C_1-C_4)alkoxycarbonyl group may include ethylcarbonyloxymethyl, 2-isopropylcarbonyloxyethyl, t-butylcarbonyloxymethyl, 2-methoxycarbonylethyl and t-butoxycarbonylmethyl group; the (C_1-C_4)alkoxy(C_1-C_4)alkyl group may include ethoxymethyl, 3-methoxypropyl, 2-ethoxyethyl and methoxymethyl group;
the di(C_1-C_4)alkylcarbamoyl group may include dimethylcarbamoyl and diethylcarbamoyl group; and
the branched (C_3-C_{10})alkyl group may include t-butyl, 1,2,2-trimethylpropyl, 2,2-dimethylpropyl and 1,2,2-trimethylbutyl group.

A preferred compound is a hydrazine derivative represented by the formula (I) as defined in claim 2.
A more preferred compound is a hydrazine derivative represented by the formula (I) as defined in claim 3.
A further preferred compound is a hydrazine derivative represented by the formula (I) as defined in claim 4.
A most preferred compound is a hydrazine derivative represented by the formula (I) according to claim 5.
The specifically preferred hydrazine derivatives are

N-(5-methylchroman-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazine,
N-cyano-N-(5-methylchroman-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazine,
N-(5-methylchroman-6-carbo)-N'-t-butyl-N'-(3,5-dimethyl-4-fluorobenzoyl)hydrazine,
N-(5-methylchroman-6-carbo)-N-trichloromethylthio-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazine,
N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-(2,2-dimethylpropyl)-N'-(3,5-dimethylbenzoyl)hydrazine,
N-cyano-N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazine,
N-(5-methyl-1,4-benzodioxan-6-carbo)-N-trichloromethylthio-N'-t-butyl-N'-(3,5-dimethylbenzoyl) hydrazine,
N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-dichlorobenzoyl)hydrazine,
N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3-difluoromethyl-5-methylbenzoyl)hydrazine,
N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-(1,2,2-trimethylpropyl)-N'-(3,5-dimethylbenzoyl)hydrazine, and
N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazine.

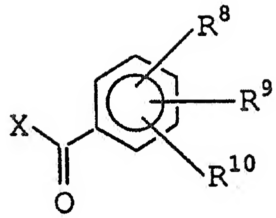
The hydrazine derivative of the formula (I) according to the present invention can be prepared by the method as mentioned below.

A hydrazide represented by the formula (II):



(II)

wherein A, B, R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^{11}, R^{12} and n have the same meanings as defined above, and a benzoyl halide represented by the formula (III):



(III)

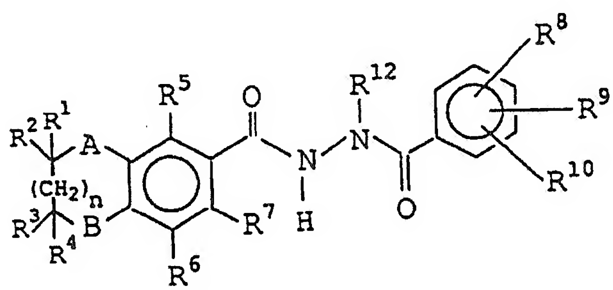
wherein R^8, R^9 and R^{10} have the same meanings as defined above, and X represents a halogen atom, are reacted in a solvent in the presence of a base to obtain the hydrazine derivative of the formula (I).

The hydrazide of the formula (II) and the benzoyl halide of the formula (III) may be reacted in an optional ratio, but preferably in an equimolar ratio or substantially equimolar ratio. As the solvent, any solvent inert to each of the reactants may be used. There may be mentioned aliphatic hydrocarbons such as hexane, heptane, etc., aromatic hydrocarbons such as benzene, toluene, xylene, etc., halogenated hydrocarbons such as chloroform, dichloromethane, chlorobenzene, etc., ethers such as diethyl ether, tetrahydrofuran, etc., nitriles such as acetonitrile, propionitrile, etc. A mixed solvent of the above or a mixed solvent of the above and water may be used. As the base, there may by used inorganic bases such as potassium hydroxide, sodium hydroxide, etc., and organic bases such as triethylamine, pyridine, etc. When organic bases such as triethylamine, pyridine, etc. are used, they may be used in large excess for use as a solvent. The base may be used in a stoichiometrical amount or in excess amount with respect to the amount of hydrogen halide to be produced during the reaction, but preferably a stoichiometrical amount or 1.0 to 5.0 time the stoichiometrical amount. The reaction can be carried out in a temperature from -20°C to the boiling point of a solvent, but preferably in the range from -5 to 50°C. A catalyst such as N,N'-dimethylaminopyridine may be added to the reaction system.

A hydrazine derivative of the formula (I) wherein R^{11} is a cyano group, $(C_1\text{-}C_4)$haloalkylthio group, $(C_2\text{-}C_5)$acyl group, di$(C_1\text{-}C_4)$alkylcarbamoyl group, $(C_1\text{-}C_4)$alkoxycarbonyl group, $(C_1\text{-}C_4)$alkoxycarbonylcarbonyl group, $(C_1\text{-}C_4)$ alkyl group which is optionally substituted by a halogen atom, $(C_1\text{-}C_4)$alkoxy group, $(C_1\text{-}C_6)$alkylcarbonyloxy group or $(C_1\text{-}C_4)$alkoxycarbonyl, group, or $(C_2\text{-}C_4)$alkenyl group, can be further obtained by.reacting a corresponding halide of the formula (IIa):

$$X\text{-}R^{11} \qquad \text{(IIa)}$$

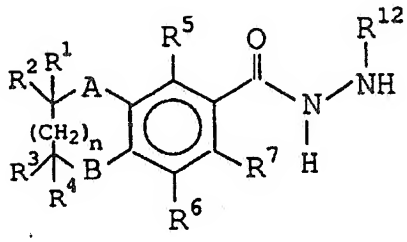
wherein X represents a halogen atom and R^{11} has the same meaning as defined above, such as cyanogen bromide, propyl bromide, halogenomethylthio halide, allyl bromide, etc. with a hydrazine derivative of the formula (Ia) (a hydrazine derivative of the formula (I) wherein R^{11} is a hydrogen atom):



(Ia)

wherein R^1 to R^{10}, R^{12}, A, B and n are the same as defined above, in an inert solvent such as tetrahydrofuran, dioxane, ether, N,N'-dimethylformamide, dimethyl sulfoxide etc. in the presence of a base such as an alkali metal hydride (sodium hydride, etc.), preferably at -10 to 50°C.

The hydrazide of the formula (IIb):

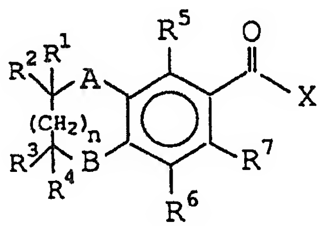


(IIb)

wherein A, B, R^1 to R^7, R^{12} and n are the same as defined above, which is used for preparing the hydrazine derivative of the formula (I) can be obtained by reacting a hydrazine represented by the formula (V):

$$R^{12}\text{-NHNH}_2\cdot\text{HCl} \quad (V)$$

wherein R^{12} is the same as defined above, with a corresponding benzoyl halide represented by the formula (IV):

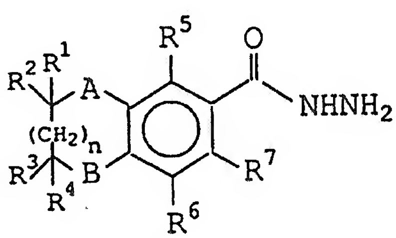


(IV)

wherein A, B, R^1, R^2, R^3, R^4, R^5, R^6, R^7, and n have the same meanings as defined above, and X is a halogen atom.

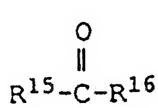
The reaction conditions such as a solvent, reaction temperature, etc. are the same as those mentioned in the reaction of the hydrazide of the formula (II) and the benzoyl halide of the formula (III).

The hydrazide of the formula (IIb) can be further obtained by a known procedure, that is, reacting a compound of the formula (VI):



(VI)

wherein A, B, R^1, R^2, R^3, R^4, R^5, R^6, R^7 and n have the same meanings as defined above, with an aldehyde of the formula (VII):

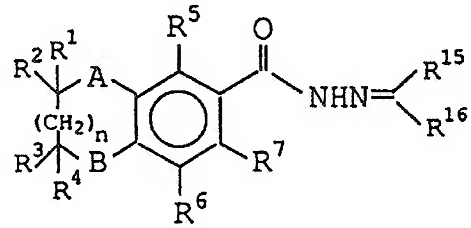


(VII)

wherein R^{15} is hydrogen atom or alkyl group and R^{16} is an alkyl group, the total carbon number of R^{15} and R^{16} being

2 to 9,

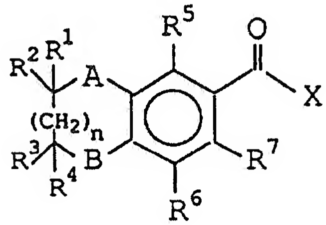
in a solvent such as alcohol (methanol, ethanol, etc.), hydrocarbon (toluene, benzene, etc.) and ether (tetrahydrofuran etc.), optionally in the presence of an organic acid such as acetic acid and trifluoroacetic acid to obtain a product of the formula (VIII):



(VIII)

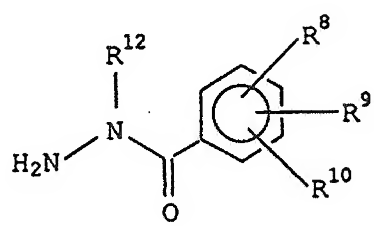
wherein A, B, R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^{15}, R^{16} and n have the same meanings as defined above, and then reducing the product of the formula (VIII) with a reducing agent such as sodium cyanoborohydride, sodium borohydride and lithium aluminum hydride, optionally in the presence of a catalyst such as acetic acid and trifluoroacetic acid in an inert solvent such as alcohols and ethers.

The compound of the formula (Ia) can be obtained by reacting the benzoyl halide represented by the formula (IV):



(IV)

wherein A, B, R^1, R^2, R^3, R^4, R^5, R^6, R^7, and n have the same meanings as defined above, and X is a halogen atom, with a hydrazide represented by the formula (IX):



(IX)

wherein R^8, R^9, R^{10},and R^{12} have the same meanings as defined above. The reaction conditions such as a solvent, reaction temperature, etc. are the same as those employed in the reaction of the hydrazide of the formula (II) and the benzoyl halide of the formula (III).

The reaction mixture when preparing the hydrazine derivative of the formula (I) or the hydrazide of the formula (II) is stirred for a sufficient time, and after usual treatments such as extraction, washing with water, drying, removal of the solvent, etc., a desired compound can be recovered. In many cases, simple washing with a solvent may be sufficient, but if necessary, recrystallization or purification by column chromatography may be carried out.

The hydrazine derivative of the formula (I) may be used as it is or as a composition in the form of various formulation such as powder, fine powder, granule, wettable powder, flowable agent, emulsifiable concentrate, microcapsule, oily agent, aerosol, heat fumigant such as mosquito-repellent incense, electric mosquito-repellent, etc., haze agent such as fogging, etc., non-heat fumigant, a poison bait, etc., according to the method generally employed in the field of pesticide formulation by using the hydrazine derivative only or mixing a pesticide adjuvant in order to enhance or stabilize the pesticidal activity depending on the use and object.

These various formulations may be used without or after diluting with water to a desired concentration for practical use.

As the pesticide adjuvant herein mentioned, there may be mentioned a carrier (a diluent) and other adjuvant such as a spreader, an emulsifier, a humectant, a dispersant, a sticking agent, a disintegrator, etc. As a liquid carrier, there may be mentioned aromatic hydrocarbons such as toluene, xylene, etc., alcohols such as butanol, octanol, glycol, etc., ketones such as acetone, etc., amides such as dimethylformamide, etc., sulfoxides such as dimethylsulfoxide, etc., methylnaphthalene, cyclohexanone, animal and vegetable oils, fatty acids, fatty acid esters, petroleum fractions such as kerosene, light oil, etc., and water.

As a solid carrier, there may be mentioned clay, kaolin, talc, diatomaceous earth, silica, calcium carbonate, montmorillonite, bentonite, feldspar, quartz, alumina, sawdust, etc.

Also, as the emulsifier or dispersant, a surfactant is usually used and there may be mentioned anionic surfactants, cationic surfactants, nonionic surfactants and amphoteric surfactants such as higher alcohol sodium sulfate, stearyltrimethylammonium chloride, polyoxyethylene alkyl phenyl ether, lauryl betain, etc.

Also, as the spreader, there may be mentioned polyoxyethylene nonyl phenyl ether, polyoxyethylene lauryl ether, etc., as the humectant, there may be mentioned polyoxyethylene nonyl phenyl ether dialkylsulfosuccinate, etc., as the sticking agent, there may be mentioned carboxymethylcellulose, polyvinyl alcohol, etc., and as the disintegrator, there may be mentioned sodium lignin sulfonate, sodium laurylsulfate, etc.

Further, two or more of the hydrazine derivative of the present invention can be combinedly formulated to exhibit more excellent pesticidal effect. Also, a multipurpose pesticidal composition having further excellent effects can be prepared by mixing other physiologically active substance such as pyrethroids including aleslin, phthalthrin, permeslin, deltameslin, fenvalerate, cycloprothrin, etc. and various isomers thereof; pyrethrum extract; organophosphorus pesticide including DDVP (dichlorvos), fenitrothion, diazinon, temephos, etc.; carbamate pesticide including NAC (carbaryl), PHC (propoxur), BPMC (Fenbucarb), pirimicarb, carbosulfun, etc.; other pesticides; acaricides; fungicides; nematicides; herbicide; plant growth regulator; fertilizers; BT agents; insect hormones; and other agricultural chemicals. By mixing such substances, synergistic effects can be also expected.

Further, by mixing a known synergist of pyrethrin such as piperonyl butoxide, sulfoxide, saphroxane, NIA-16824 (O-sec-butyl O-propargyl phenylphosphonate), DEF (S, S, S, - tributylphosphotrithioate), etc., the pesticidal effect of the hydrazine derivative can be enhanced.

The hydrazine derivative of the present invention has high stability to light, heat, oxidation, etc., but depending on necessity, antioxidants or UV-absorbers such as phenols including BHT, BHA, etc., arylamines such as α-naphthylamine and benzophenone compounds may be mixed as a stabilizer to obtain a composition having more stable effects.

The amount of the effective ingredient (the hydrazine derivative) in the pesticidal composition of the present invention may vary depending on formulation, method of application and other conditions, and the hydrazine derivative alone may be used in some case, but generally in the range from 0.02 to 95 % by weight, preferably 0.05 to 80 % by weight.

The application amount of the pesticidal composition of the present invention may vary depending on the formulation, method or time of application and other conditions, but for agricultural and horticultural purpose and for controlling pest in forest, field, garden and post harvest, the pesticidal composition may be applied 0.5 to 300 g, preferably 2 to 200 g per 10 ares based on the amount of the effective ingredient. Also, in case of controlling sanitary insect pest, the application amount of the pesticidal composition is usually in the range from 1 to 200 mg, preferably 1 to 100 mg per 1 m^2 based on the amount of the effective ingredient. For example, from 1 to 120 g per 10 ares for a powder agent, from 5 to 300 g per 10 ares for a granule, from 0.5 to 100 g for an emulsifiable concentrate, wettable powder, flowables, water dispersible granules and emulsion in water, all based on the amount of the effective ingredient. However, in a specific case, it may exceed or lower the above ranges and is necessary in some cases.

Also, when the hydrazine derivative of the formula (I) according to the present invention is used for controlling parasite, it may be used with an administration dose from 0.1 to 200 mg/kg based on the body weight. An accurate administration dose to the given state can be daily determined depending on various factors such as a hydrazine derivative to be used, kinds of parasite, kinds of formulation to be used and conditions of human or animal suffering from parasitic disease.

Specific harmful pests to which the pesticidal composition of the present invention can be applied are mentioned below.

Hemiptera: Nephotettix cincticeps, Sogatella furcifera, Nilaparvata lugens, Laodelphax striatellus, Riptortus clavatus, Nezara viridula, Stephanitis nashi, Trialeurodes vaporariorum, Aphis gassypii, Myzus persicae, Unasqis yanonensis

Lepidoptera: Phyllonorycter ringoneella, Plutella xylostella, Promalactis inonisema, Adoxophyes orana, Leguminivora glycinivorella, Cnaphalocrocis medinalis, Chilo supperessalis, Ostrinia furnacalis, Mamestra brassicae, Pseudaletia separata, Spodoptera litura, Parnara guttata, Pieris rapae-crucivora, Heliothis spp., Agrotis spp., Helicov-

erpa spp.
Coleoptera: Anomala cuprea, Popillia japonica, Echinocnemus sogameus, Lissorhoptrus oryzophilus, Oulema oryzae, Anthrenus verbasic, Tenebroides mauritanicus, Sitophilus zeamis, Henosepilachna vigintioctopunctata, Callosobruchus chinensis, Monochamus alternatus, Aulacophora femoralis, Leptiontarsa decemlineta, Phaedon cochlearias, Diabrotica spp.
Hymenoptera: Athalia rosae japonensis, Argesimilis
Diptera: Culex pipiens fatigans, Aedes aegypti, Asphondylls sp., Hylemya platura, Musca domestica viclna, Dacus cucurcitae, Agromyza oryzae, Lucllia spp.
Aphaniptera, there may be mentioned *Pulex irritans, Xenopsylla cheopis, Ctenocephalides canis*
Thysanoptera, there may be mentioned *Scirtothrips dorsalls, Thrips tabaci, Thrips palmi, Baliothrips biformis*
Anoplura: Pediculs humanus corporis, Pthirus pubis
Psocoptera: Trogium pulsatorium, Liposcelis bostrychophilus
Orthoptera: Gryllotalpa africana, Locusta migratoria, Oxya yezoensis, Blattella germanlica, Periplaneta fuliginosa.

Also, the most general parasite which damages human and the diseases caused by them to which the pesticidal composition of the present invention can be applied are summarized below but the application of the present invention is not limited by these.

Name of disease	Parasite
Bilharziosis or *Schistosomiasis*	*Schistosoma mansoni, S. Japonicum, S. Haematobium*
Ancyclostomiasis	*Necator americanus, Ancyclostoma duodenale*
Ascariasis	*Ascaris lumbricoldes*
Filariasis or *elephantiasis*	*Wuchereria bancrofti, Brugia malayi*
Onchoceriasis or *river blinduess*	*Onchocerrca volvulus,*
Loiasis	*Loa loa*

In the following, the present invention is described in more detail by referring to examples, but the present invention is not limited by these examples.

Synthetic Example 1:

Production of N-(5-methyl-1,4-benzodioxan-6-carbo) -N'-(1,2,2-trimethylpropyl)hydrazine:

In 10 ml of methanol, was dissolved 0.37 g of N-5-methyl-1,4-benzodioxan-6-carbohydrazide, and a catalytic amount of acetic acid was added thereto and 0.20 g of pinacolone was added dropwise to the mixture. After stirring at room temperature for 3 hours, 0.21 g of acetic acid and 0.22 g of sodium cyano boron hydride were successively added to the mixture and the mixture was stirred at room temperature for 8 hours. The reaction mixture was poured into a 5 % aqueous sodium hydroxide solution, and methanol was removed under reduced pressure and the residue was extracted by ethyl acetate. The ethyl acetate layer was washed successively with a diluted sodium hydroxide aqueous solution, water and then saturated saline solution, dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure to obtain 0.47 g (yield: 90 %) of the titled N-5-methyl-1,4-benzodioxan-6-carbo-N'-1,2,2-trimethylpropylhydrazine.

^{1}H-NMR ($CDCl_3$) δ (ppm):

0.98 (9H, s), 1.07 (3H, d, J=6.6Hz), 2.27 (3H, s), 2.74 (1H, q, J=6.6Hz), 4.26 (4H, s), 6.68 (1H, d, J=8.2Hz), 6.87 (1H, d, J=8.2Hz), 7.80 (1H, brs)

Synthetic Example 2:

Production of N-5-methyl-1,4-benzodioxan-6-carbohydrazine:

In 4 ml of thionyl chloride, was dissolved 0.53 g of 5-methyl-1,4-benzodioxan-6-carboxylic acid and the solution

was refluxed under heating for one hour. Excessive thionyl chloride was distilled off and the residue was dissolved in 3 ml of methylene chloride. To a mixed solution of 10 ml of methylene chloride and 2 ml of water, was added 1.4 g of hydrazine hydrate, and the previously prepared methylene chloride solution of 5-methyl-1,4-benzodioxan-6-carbonyl chloride was added dropwise to the mixture under cooling with ice.

After returned to room temperature and stirring for one hour, the mixture was poured into water and extracted with methylene chloride. The methylene chloride layer was washed successively with water and saturated saline solution, dried over anhydrous magnesium sulfate, condensed under reduced pressure to obtain 0.41 g (yield: 72 %) of the titled N-5-methyl-1,4-benzodioxan-6-carbohydrazine.

^{1}H-NMR ($CDCl_3$) δ(ppm):

2.28 (3H, s), 3.74 (2H, brs), 4.27 (4H, s), 6.71 (1H, d, J=8.3Hz), 6.92 (1H, d, J=8.3Hz)

Synthetic Example 3:

Production of N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-(1,2,2-trimethylpropyl)-N'-(3,5-dimethylbenzoyl)hydrazine (Example No. 1-2):

In 8 ml of pyridine, was dissolved 0.43 g of N-5-methyl-1,4-benzodioxan-6-carbo-N'-1,2,2-trimethylpropylhydrazine and a catalytic amount of 4-dimethylaminopyridine (DMAP) was added to the solution, and 0.27 g of 3,5-dimethylbenzoyl chloride was added dropwise under cooling with ice.

After stirring at room temperature for 4 hours, the mixture was poured into water and extracted with ethyl acetate. The ethyl acetate layer was washed successively with a 5 % hydrochloric acid, water and saturated saline solution, dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The resulting crystals were recrystallized from a mixed solvent of ethyl acetate and diethyl ether to obtain 0.48 g of the titled N-5-methyl-1,4-benzodioxan-6-carbo-N'-1,2,2-trimethylpropylN'-3,5-dimethylbenzoylhydrazine (yield: 78 %).

^{1}H-NMR ($CDCl_3$) δ(ppm):

1.04 (9H, s), 1.29 (3H, d, J=6.3Hz), 2.29 (9H, s), 4.22 (4H, s), 4.92 (1H, q, J=6.3Hz), 6.28 (1H, d, J=8.2Hz), 6.61 (1H, d, J=8.2Hz), 7.00-7.12 (4H, m)

Synthetic Example 4

Production of N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazine (Example No. 1-5):

In 15 ml of pyridine, were dissolved 0.83 g of N-t-butyl-N'-3,5-dimethylbenzoylhyrazine and a catalytic amount of DMAP and after cooling the solution to 0°C, 0.80 g of 5-methyl-1,4-benzodioxan-6-carbonyl chloride was added dropwise to the solution. After stirring for 2 hours, water was added to the mixture and the mixture was extracted with ethyl acetate. The resulting ethyl acetate layer was washed successively with a 5 % hydrochloric acid, water and saturated saline solution, dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The resulting crystals were recrystallized from a mixed solvent of ethyl acetate and diethyl ether to obtain 0.61 g of the titled N-5-methyl-1,4-benzodioxan-6-carbo-N'-t-butyl-N'-3,5-dimethylbenzoylhydrazine (yield: 46 %).

^{1}H-NMR ($CDCl_3$) δ(ppm):

1.58 (9H, s), 1.94 (3H, s), 2.25 (6H, s), 4.21 (4H, s), 6.12 (1H, d, J=8.3Hz), 6.52 (1H, d, J=8.3Hz), 6.98 (1H, s), 7.04 (2H, s), 7.50 (1H, brs).

Synthetic Example 5:

Production of 5-methyl-1,4-benzodioxane

In 300 ml of dry dimethylformamide, was dissolved 30 g of 3-methylcatechol and then 100 g of potassium carbonate was added to the solution. This solution was heated to 120 to 130°C and 136 g of 1,2-dibromoethane was added dropwise in ten and several portions. After stirring for 30 minutes under the same conditions, the mixture was cooled and solid materials were removed by filtration. To the filtrate, was added diethyl ether, and the mixture was washed successively with a 3 % sodium hydroxide aqueous solution, water and saturated saline solution, dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The resulting oily material was purified by silica gel column chromatography to obtain 29.7 g of the titled 5-methyl-1,4-benzodioxane (yield: 82 %).

^{1}H-NMR ($CDCl_3$) δ (ppm):

2.19 (3H, s), 4.24 (4H, s), 6.71 (3H, s)

Synthetic Example 6:

Production of 6-bromo-5-methyl-1,4-benzodioxane:

In 30 ml of acetic acid, was dissolved 10 g of 5-methyl-1,4-benzodioxane and 11.8 g of bromine was added dropwise to the solution. After stirring for 30 minutes, the reaction mixture was poured into a sodium hydrogen sulfite aqueous solution and extracted with diethyl ether. The resulting diethyl ether layer was washed successively with a sodium hydrogen carbonate aqueous solution, water and saturated saline solution, dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure to obtain 15.0 g of 6-bromo-5-methyl-1,4-benzodioxane (bp. 126-135°C (7 mmHg)).

^{1}H-NMR ($CDCl_3$) δ(ppm):

2.25 (3H, s), 4.23 (4H, s), 6.60 (1H, d, J=8.9Hz), 6.99 (1H, d, J=8.9Hz)

Synthetic Example 7:

Production of 5-methyl-1,4-benzodioxan-6-carboxylic acid:

In 300 ml of dry tetrahydrofuran, was dissolved 32.0 g of 6-bromo-5-methyl-1,4-benzodioxane and after cooling the solution to -78°C, 96.7 ml of n-butyl lithium (n-hexane solution) was added dropwise over 20 minutes or more. After stirring at the same temperature for 1.5 hours, the reaction mixture was poured onto crushed dry ice and dry ice was sublimated while stirring. Water was added to the mixture and the tetrahydrofuran was removed under reduced pressure. The resulting alkaline aqueous solution was washed with methylene chloride and adjusted to pH 3 with a 5 % hydrochloric acid, and the precipitated crystals were collected by filtration and dried to obtain 20.9 g of 5-methyl-1,4-benzodioxan-6-carboxylic acid (yield: 77 %).

^{1}H-NMR ($CDCl_3$) δ(ppm):

2.51 (3H, s), 4.29 (4H, s), 6.76 (1H, d, J=9.9Hz), 7.62 (1H, d, J=9.9Hz), 11.98 (1H, brs)

Synthetic Example 8:

Production of 5-methyl-1,4-benzodioxan-6-carbaldehyde:

In 100 ml of dry tetrahydrofuran, was dissolved 3.3 g of N,N,N'-trimethylethylenediamine and to the solution was added dropwise 19.2 ml of n-butyl lithium (1.59 mol/l, n-hexane solution) at -20°C. After stirring at -20°C for 15 minutes, to the mixture was added dropwise 5.0 g of 1,4-benzodioxan-6-carbaldehyde dissolved in 7 ml of dry tetrahydrofuran and the mixture was stirred for 15 minutes. Then, 57.5 ml of n-butyl lithium (1.59 mol/l, n-hexane solution) was further added dropwise to the mixture and the mixture was stirred at -20°C for 3 hours. Thereafter, the mixture was cooled to -42°C and 25.9 g of methyl iodide was added dropwise, and the mixture was stirred at the same temperature for 4 hours and poured into an ice-cooled 5% hydrochloric acid. The tetrahydrofuran was removed under reduced pressure and the mixture was extracted with diethyl ether, and the resulting diethyl ether layer was washed successively with water and saturated saline solution, and dried over anhydrous magnesium sulfate.

The solvent was removed under reduced pressure and the resulting oily material was purified by silica gel column chromatography to obtain 0.8 g of the titled 5-methyl-1,4-benzodioxan-6-carbaldehyde (yield: 15 %).

^{1}H-NMR ($CDCl_3$) δ(ppm):

2.52 (3H, s), 4.31 (4H, s), 6.83 (1H, d, J=8.5Hz), 7.35 (1H, d, J=8.5Hz), 10.10 (1H, s)

Synthetic Example 9:

Production of 5-methyl-1,4-benzodioxan-6-carboxylic acid:

In 5 ml of tetrahydrofuran was dissolved 0.8 g of 5-methyl-1,4-benzodioxan-6-carbaldehyde, then 27 ml of a 1% sodium hydroxide aqueous solution was added dropwise to the solution and further 0.5 g of a 10% palladium-carbon was added thereto, and the mixture was refluxed under heating for 1.5 days. The mixture was cooled to room temperature, 10 ml of a 10% sodium sulfite aqueous solution was added thereto and after stirring for 30 minutes, the mixture was filtered and the tetrahydrofuran was removed under reduced pressure. The residue was adjusted to pH 3 with a 5% hydrochloric acid and extracted with diethyl ether. The diethyl ether layer was washed successively with water and saturated saline solution and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to obtain 0.53 g of the titled 5-methyl-1,4-benzodioxan-6-carboxylic acid (yield: 61 %).

^{1}H-NMR ($CDCl_3$) δ(ppm):

2.51 (3H, s), 4.29 (4H, s), 6.76 (1H, d, J=8.6Hz), 7.62 (1H, d, J=8.6Hz), 11.98 (1H, brs)

Synthetic Example 10:

Production of N-5-methylchroman-6-carbo-N'-t-butylhydrazine:

In toluene, was suspended 3.3 g of 5-methylchroman-6-carboxylic acid and to the suspension were added 2.5 ml of thionyl chloride and a catalytic amount of N,N-dimethylformamide, and the mixture was stirred at 80°C for 2 hours. The excessive thionyl chloride and the toluene were removed by distillation, and the residue was dissolved in 10 ml of methylene chloride. To 30 ml of a methylene chloride solution containing 6.4 g of t-butylhydrazine hydrochloride, was added 34 g of a 10% sodium hydroxide aqueous solution under cooling with ice and to the mixture was further added dropwise the previously prepared methylene chloride solution of 5-methylchroman-6-carbonyl chloride. After stirring for 30 minutes, the mixture was poured into water and extracted with methylene chloride. The methylene chloride layer was washed with saturated saline solution and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue obtained was washed with diethyl ether to obtain 3.7 g of the titled N-5-methylchroman-6-carbo-N'-t-butylhydrazine (yield: 82 %).

^{1}H-NMR ($CDCl_3$) δ(ppm):

7.12 and 6.65 (d, 2H), 5.60 (brs, 2H), 4.14 (t, 2H), 2.66 (t, 2H), 2.29 (s, 3H), 2.04 (q, 2H), 1.16 (s, 9H)

Synthetic Example 11:

Production of N-(5-methylchroman-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazine (Example No. 1-15):

In 20 ml of pyridine, was dissolved 3.7 g of N-5-methylchroman-6-carbo-N'-t-butylhydrazine and to the solution was added a catalytic amount of 4-dimethylaminopyridine, and then 2.85 g of 3,5-dimethylbenzoyl chloride was added dropwise to the mixture under cooling with ice. After stirring at room temperature for 2 hours, the mixture was poured into water and extracted with ethyl acetate. The ethyl acetate layer was washed with a 5% hydrochloric acid and saturated saline solution, and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the resulting crystals were washed with diethyl ether to obtain 5.0 g of the titled N-5-methylchroman-6-carbo-N'-t-butyl-N'-3,5-dimethylbenzoylhydrazine (yield: 90 %).

^{1}H-NMR ($CDCl_3$) δ(ppm):

7.43 (s, 1H), 7.05 and 6.98 (bs, 3H), 6.44 and 6.37 (d, 2H), 4.15 (t, 2H), 2.56 (t, 2H), 2.26 (s, 6H), 1.98 (m, 2H), 1.95 (s, 3H), 1.59 (s, 9H)

Synthetic Example 12:

Production of N-cyano-N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazine (Example No. 1-139):

A solution of N-5-methyl-1,4-benzodioxan-6-carbo-N'-t-butyl-N'-3,5-dimethylbenzoylhydrazine (300 mg) in tetrahydrofuran (6 ml) was treated slowly with 60% sodium hydride (50 mg) at room temperature. After 15 minutes, a solution of cyanogen bromide (135 mg) in tetrahydrofuran (2 ml) was added dropwise, the reaction mixture was refluxed for 1 hr, poured into cold water, and then extracted with ethyl ether. The organic layer was washed with water and saturated aqueous NaCl. After the extracts were dried over anhydrous magnesium sulfate, evaporation of solvents gave an oil which was chromatographed on silica gel to give 256 mg of N-cyano-N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazine as a pale yellow amorphous.

^{1}H-NMR ($CDCl_3$) δ(ppm):

1.69 (9H, s), 1.84 (3H, s), 2.31 (6H, s), 4.22-4.27 (4H, m), 6.10 (1H, d, J=8.5 Hz), 6.59 (1H, d, J=8.5 Hz), 7.08 (1H, s), 7.13 (2H, s)

Synthetic Example 13:

Production of N-(dimethylcarbamoyl)-N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl) hydrazine (Example No. 1-84):

To a suspension of 60% sodium hydride (428 mg) in dimethylformamide (15 ml) at room temperature was added dropwise a solution of N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-3,5-dimethylbenzoylhydrazine (1.01 g) in dimethylformamide (5 ml). The resulting suspension was stirred at room temperature for 30 min, and dimethylcarbamoyl

chloride (0.94 ml) was added and stirred at room temperature for 15 min, and then stirred at 100°C for 2 hrs.

The reaction mixture was poured into cold water, and then extracted with ethyl acetate. The organic layer was washed with water and saturated aqueous NaCl. After the extracts were dried over anhydrous magnesium sulfate, evaporation of the solvents gave an oil which was chromatographed on silica gel to give 225 mg of N-(dimethylcarbamoyl)-N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazine as a solid (mp = 60-64°C).

^{1}H-NMR ($CDCl_3$) δ(ppm):

1.56 (9R, s), 2.24 (3H, s), 2.36 (6H, s), 2.55-2.75 (3H, brs), 2.80-3.05 (3H, brs), 4.20-4.27 (4H, m), 6.61 (1H, d, J=8.4 Hz), 7.12 (1H, s), 7.21 (1H, d, J=8.4 Hz), 7.66 (2H, s)

Representative examples of the hydrazine derivative according to the present invention are shown in the following tables.

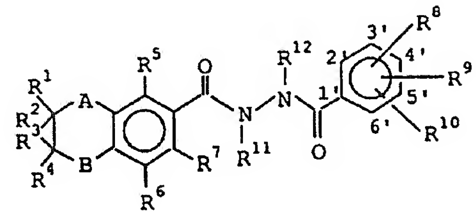


Table 1

No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
1-1	O	O	H	H	H	H	Me	H	H	2'-Cl	H	5'-Me	H	$-CMe_3$	237-238
1-2	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CH(CMe_3)-Me$	237-238
1-3	O	O	H	H	H	H	Me	H	H	H	H	H	H	$-CMe_3$	189-192
1-4	O	O	H	H	H	H	Me	H	H	2'-I	H	H	H	$-CMe_3$	215-216
1-5	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	129-131
1-6	O	O	H	H	H	H	Me	H	H	2'-Cl	H	5'-Me	H	$-CH(CMe_3)-Me$	179-180
1-7	O	O	H	H	H	H	Me	H	H	H	3'-Me	H	H	$-CH(CMe_3)-Me$	172-174
1-8	O	$-CH_2-$	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	124-126
1-9	O	O	H	H	H	H	Br	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	274-275

Table 2

No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
1-10	O	O	H	H	H	H	NO_2	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	224-225
1-11	O	O	H	H	H	H	NH_2	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	226-227
1-12	O	CH_2	Me	Me	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	118-120
1-13	O	O	H	H	H	H	Me	H	H	2'-Cl	4'Cl	H	H	$-CMe_3$	Amorphous
1-14	O	O	H	H	H	H	Me	H	H	H	3'-Me	$5'-CH_2OSi(Me)_2-Bu(t)$	H	$-CMe_3$	Amorphous
1-15	CH_2	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	114-116
1-16	CH_2	O	H	H	Me	Me	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	125-127
1-17	O	O	H	H	H	H	F	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	234-235
1-18	$-C(=O)-$	O	H	H	H	H	H	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	247-248
1-19	O	O	H	H	H	H	Me	H	H	$2'-NO_2$	H	H	H	$-CMe_3$	Amorphous
1-20	O	O	H	H	H	H	Me	H	H	H	3'-Me	$5'-CH_2OH$	H	$-CMe_3$	127-129
1-21	O	O	H	H	H	H	Me	H	H	H	3'-Cl	5'-Cl	H	$-CMe_3$	254-256
1-22	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-CHO	H	$-CMe_3$	203-205
1-23	O	O	H	H	H	H	Me	H	H	H	3'-Me	$5'-CH_2F$	H	$-CMe_3$	113-115

Table 3

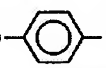
No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
1-24	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-CHF_2	H	$-CMe_3$	100-103
1-25	O	O	H	H	H	H	Me	H	H	2'-NO_2	H	5'-Me	H	$-CMe_3$	212-214
1-26	O	O	H	H	H	H	Me	H	H	2'-NO_2	3'-Me	H	H	$-CMe_3$	165-168
1-27	O	O	H	H	H	H	Me	H	H	H	3'-OMe	H	H	$-CMe_3$	92-95
1-28	O	O	H	H	H	H	Me	H	H	2'-Cl	3'-Cl	5'-Cl	H	$-CMe_3$	201-204
1-29	O	O	H	H	H	H	Me	H	H	H	H	3'-O-CH_2CH_2O--F	H	$-CMe_3$	195-198
1-30	O	O	H	H	H	H	Me	H	H	2'-NO_2	3'-Me	5'-Me	H	$-CMe_3$	202-203
1-31	O	O	H	H	H	H	CH_2Br	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	119-120
1-32	O	O	H	H	H	H	$C_3H_7(i)$	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	158-160
1-33	O	O	H	H	H	H	H	$C_3H_7(i)$	H	H	3'-Me	5'-Me	H	$-CMe_3$	236-7
1-34	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	$-CH_2OC(=O)-Bu(t)$	$-CH(CMe_3)-Me$	Amorphous
1-35	CH_2	O	H	H	H	H	Me	Cl	H	H	3'-Me	5'-Me	H	$-CMe_3$	204-207
1-36	CH_2	O	H	H	H	H	Me	Me	H	H	3'-Me	5'-Me	H	$-CMe_3$	138-140
1-37	CH(OMe)	O	H	H	H	H	H	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	203-204

Table 4

No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
1-38	$>CH-OMe$	O	H	H	H	H	H	H	H	H	3'-Cl	5'-Cl	H	$-CMe_3$	191-192
1-39	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	$-C(=O)-C(=O)-OEt$	$-CH(Me)-CMe_3$	Amorphous
1-40	O	O	H	H	H	H	Me	H	H	H	3'-Cl	5'-Cl	H	$-CH(Me)-CMe_3$	208-209
1-41	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-CH=CH_2	H	$-CMe_3$	Amorphous
1-42	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-C_2H_5	H	$-CMe_3$	Amorphous
1-43	O	O	H	H	H	H	CH_2F	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	105-109
1-44	O	O	H	H	H	H	CHF_2	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	186-189
1-45	$-CH(-O-CH_2-C_6H_4-F)-$	O	H	H	H	H	H	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	193-194
1-46	O	O	H	H	H	H	C_2H_5	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	108-111
1-47	S	O	H	H	H	H	H	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	250-252

Table 5

No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
1-48	CH_2	O	H	H	H	H	F	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	203-205
1-49	CH_2	O	H	H	H	H	H	F	H	H	3'-Me	5'-Me	H	$-CMe_3$	
1-50	CH_2	O	H	H	H	H	H	H	F	H	3'-Me	5'-Me	H	$-CMe_3$	174-175
1-51	O	O	Me	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	128-130
1-52	O	O	H	H	Me	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	203-205
1-53	O	$>C=O$	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	201-203
1-54	O	O	$MeOCH_2-$	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	124-126
1-55	O	O	$C_6H_5-CH_2OCH_2$	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	196-198
1-56	O	O	H	H	H	H	Me	Br	H	H	3'-Me	5'-Me	H	$-CMe_3$	Amorphous
1-57	O	O	H	H	H	H	$-CH=CH_2$	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	97-100
1-58	O	O	H	H	H	H	$-CH_2SMe$	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	85-87
1-59	O	O	H	H	H	H	Me	H	H	2'-NO_2	H	5'-Cl	H	$-CMe_3$	200-203
1-60	O	O	H	H	H	H	Me	Me	H	H	3'-Me	5'-Me	H	$-CMe_3$	122-124
1-61	O	O	H	H	H	H	Me	H	NO_2	H	3'-Me	5'-Me	H	$-CMe_3$	222-224
1-62	CH_2	O	H	H	H	H	Me	H	H	H	3'-Cl	5'-Cl	H	$-CMe_3$	193-195

Table 6

No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
1-63	CH_2	O	H	H	H	H	Me	H	H	3'-Me	4'-F	5'-Me	H	$-CMe_3$	216-218
1-64	CH_2	O	H	H	H	H	Me	H	H	2'-Cl	H	5'-Me	H	$-CMe_3$	217-220
1-65	CH_2	O	H	H	H	H	Me	H	H	2'-Cl	4'-F	5'-Me	H	$-CMe_3$	190-191
1-66	CH_2	O	H	H	H	H	H	Me	H	H	3'-Me	5'-Me	H	$-CMe_3$	Amorphous
1-67	O	O	H	H	H	H	Me	H	Cl	H	3'-Me	5'-Me	H	$-CMe_3$	133-134
1-68	O	O	H	H	H	H	Me	Cl	H	H	3'-Me	5'-Me	H	$-CMe_3$	Amorphous
1-69	O	O	H	H	H	H	$-CH_2OMe$	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	78-81
1-70	O	O	H	H	H	H	CN	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	264-266
1-71	O	O	H	H	H	H	Me	H	H	$2'-NO_2$	3'-Cl	H	H	$-CMe_3$	87-91
1-72	O	O	H	H	H	H	$-CH{=}CH-CH_3$	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	95-99
1-73	O	O	H	H	H	H	Pr(n)	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	93-95
1-74	CH_2	O	H	H	H	H	Me	H	H	$2'-NO_2$	H	H	H	$-CMe_3$	212-214
1-75	O	-CH(OMe)-	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	113-116
1-76	O	O	H	H	H	H	Cl	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	271-273
1-77	O	O	H	H	H	H	OMe	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	155-157

Table 7

No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
1-78	O	O	H	H	H	H	Me	H	Me	H	3'-Me	5'-Me	H	$-CMe_3$	
1-79	O	O	H	H	H	H	H	H	Me	H	3'-Me	5'-Me	H	$-CMe_3$	240-242
1-80	O	O	H	H	H	H	Me	H	F	H	3'-Me	5'-Me	H	$-CMe_3$	254-256
1-81	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	$COCH_3$	$-CMe_3$	Amorphous
1-82	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	Me	$-CMe_3$	76-78
1-83	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	$CON(Me)_2$	$-CMe_3$	60-64
1-84	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	CH_2CH_2OEt	$-CMe_3$	92-94
1-85	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	CH_2OEt	$-CMe_3$	65-68
1-86	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	$CH_2CH{=}CH_2$	$-CMe_3$	Amorphous
1-87	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	$SCCl_3$	$-CMe_3$	Amorphous
1-88	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	COOBu(iso)	$-CMe_3$	Amorphous
1-89	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	$CH_2CH_2CH_2Br$	$-CMe_3$	Amorphous
1-90	CH_2	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	$SCCl_3$	$-CMe_3$	87-90
1-91	O	O	H	H	H	H	Me	H	H	3'-Me	4'-F	5'-Me	H	$-CMe_3$	245-246
1-92	O	O	H	H	H	H	Me	H	H	2'-Cl	4'-F	5'-Me	H	$-CMe_3$	133-135

Table 8

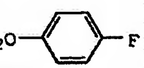
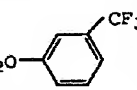
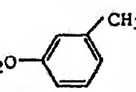
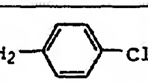
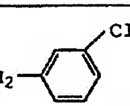
No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
1-93	O	O	H	H	H	H	Me	H	H	2'-Br	4'-F	H	H	$-CMe_3$	207-208
1-94	O	O	H	H	H	H	Me	H	H	H	H	$3'-OCF_3$	H	$-CMe_3$	224-225
1-95	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-OMe	H	$-CMe_3$	218-220
1-96	O	O	H	H	H	H	Me	H	H	H	H	3'-C≡CH	H	$-CMe_3$	130-133
1-97	O	O	H	H	H	H	Me	H	H	$2'-SCF_3$	H	H	H	$-CMe_3$	197-199
1-98	O	O	H	H	H	H	Me	H	H	$2'-CF_3$	H	H	H	$-CMe_3$	212-213
1-99	O	O	H	H	H	H	Me	H	H	H	3'-Me	$5'-O-CH_2CH_2O-$ 	H	$-CMe_3$	158-160
1-100	O	O	H	H	H	H	Me	H	H	H	3'-Me	$5'-O-CH_2CH_2O-$ 	H	$-CMe_3$	160-161
1-101	O	O	H	H	H	H	Me	H	H	H	3'-Me	$5'-O-CH_2CH_2O-$ 	H	$-CMe_3$	Amorphous
1-102	O	O	H	H	H	H	Me	H	H	H	3'-Me	$5'-OCH_2CH_2-$ 	H	$-CMe_3$	176-177
1-103	O	O	H	H	H	H	Me	H	H	H	3'-Me	$5'-OCH_2-$ 	H	$-CMe_3$	07-209
1-104	O	O	H	H	H	H	Me	H	H	H	3'-Me	$5'-OCH_2CF_3$	H	$-CMe_3$	Amorphous

Table 9

No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
1-105	-CH(Me)-	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	
1-106	-C(=O)-	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	133-136
1-107	-CH(OH)-	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	234-237
1-108	>C=N-OMe	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	236-240
1-109	O	>CH-Me	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	
1-110	$-CH_2-$	O	H	H	H	H	Me	H	H	2'-Br	4'-F	H	H	$-CMe_3$	208-209
1-111	$-CH_2-$	O	H	H	H	H	Me	H	H	H	H	4'-Bu(t)	H	$-CMe_3$	270-272
1-112	$-CH_2-$	O	H	H	H	H	Me	H	H	H	H	$3'-OCF_3$	H	$-CMe_3$	197-200
1-113	$-CH_2-$	O	H	H	H	H	Me	H	H	2'-I	H	H	H	$-CMe_3$	237-239
1-114	$-CH_2-$	O	H	H	H	H	Me	H	H	$2'-SCF_3$	H	H	H	$-CMe_3$	150-152
1-115	$-CH_2-$	O	H	H	H	H	Me	H	H	H	H	3'-CHO	H	$-CMe_3$	220-223
1-116	$-CH_2-$	O	H	H	H	H	Me	H	H	H	3'-Me	5'-OMe	H	$-CMe_3$	110-115

Table 10

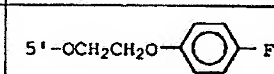
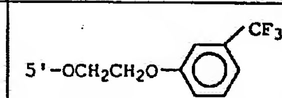
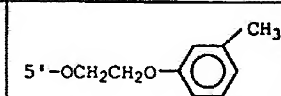
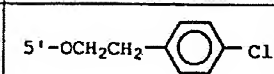
No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
1-117	$-CH_2-$	O	H	H	H	H	Me	H	H	H	3′-Me	5′-Me	H	$-CH(Me)-CMe_3$	179-180
1-118	$-CH_2-$	O	H	H	H	H	Me	H	H	H	3′-Cl	5′-Cl	H	$-CH(Me)-CMe_3$	190-191
1-119	$-CH_2-$	O	H	H	H	H	Me	H	H	2′-Cl	4′-Cl	H	H	$-CH(Me)-CMe_3$	113-116
1-120	$-CH_2-$	O	H	H	H	H	Me	H	H	$2'-NO_2$	H	H	H	$-CH(Me)-CMe_3$	Amorphous
1-121	$-CH_2-$	O	H	H	H	H	H	H	Me	H	3′-Me	5′-Me	H	$-CMe_3$	202-204
1-122	$-CH_2-$	O	H	H	H	H	Me	H	H	H	3′-Me		H	$-CMe_3$	137-139
1-123	$-CH_2-$	O	H	H	H	H	Me	H	H	H	3′-Me		H	$-CMe_3$	158-160
1-124	$-CH_2-$	O	H	H	H	H	Me	H	H	H	3′-Me		H	$-CMe_3$	Amorphous
1-125	$-CH_2-$	O	H	H	H	H	Me	H	H	H	3′-Me		H	$-CMe_3$	169-171

Table 11

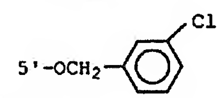
No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
1-126	$-CH_2-$	O	H	H	H	H	Me	H	H	H	3'-Me		H	$-CMe_3$	185-187
1-127	$-CH_2-$	O	H	H	H	H	Me	H	H	H	3'-Me	5'-OCH_2CF_3	H	$-CMe_3$	Amorphous
1-128	Me | -N-	O	H	H	H	H	H	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	248-251
1-129	Ac | -N-	O	H	H	H	H	H	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	232-235
1-130	O	-N- | Me	H	H	H	H	H	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	249-250
1-131	H -N-	O	H	H	H	H	H	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	248-252
1-132	O	-N- | Ac	H	H	H	H	H	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	120-122
1-133	O	-N- H	H	H	H	H	H	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	225-227
1-134	O	O	H	H	H	H	CH_3	H	H	2'-F	H	H	H	$-CMe_3$	158-159
1-135	O	O	H	H	H	H	CH_3	H	H	H	3'-Cl	4'-Cl	H	$-CMe_3$	258-259
1-136	O	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-CH_3	H	$-CH_2-CMe_3$	182-184

Table 12

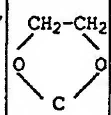
No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
1-137		O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-CH_3	H	-CMe_3	243-244
1-138	O	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-CH_3	CN	-CMe_3	Amorphous
1-139	O	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-CH_3	-$CH_2C(=O)OBu$(t)	-CMe_3	-193 (Sublimed)
1-140	O	O	H	H	H	H	CH_3	Cl	Cl	H	3'-CH_3	5'-CH_3	H	-CMe_3	165-170
1-141	O	O	H	H	H	H	CH_3	H	Br	H	3'-CH_3	5'-CH_3	H	-CMe_3	250-252
1-142	O	O	H	H	H	H	CH_3	$CHCl_2$	H	H	3'-CH_3	5'-CH_3	H	-CMe_3	222-224
1-143	O	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-$OCH_2CH=CH_2$	H	-CMe_3	162-165
1-144	O	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-$OCH_2C{\equiv}CH$	H	-CMe_3	Amorphous
1-145	CH_2	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-$OCH_2CH=CH_2$	H	-CMe_3	129-131
1-146	CH_2	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-$OCH_2C{\equiv}CH$	H	-CMe_3	Amorphous
1-147	CH_2	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-CH_3	-$COCH_3$	-CMe_3	Amorphous
1-148	O	O	H	H	H	H	CH_3	H	H	H	H	3'-OCH_2CH_2OEt	H	-CMe_3	147-150
1-149	O	O	H	H	H	H	CH_3	H	H	H	H	3'-OCH_2CH_2Br	H	-CMe_3	136-140
1-150	CH_2	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-CH_3	-CH_2-$CH=CH_2$	-CMe_3	Amorphous
1-151	CH_2	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-CH_3	-CH_2CH_2OEt	-CMe_3	Amorphous

Table 13

No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
1-152	CH_2	O	H	H	H	H	CH_3	H	H	H	H	3'-OCH_2CH_2OEt	H	$-CMe_3$	146-148
1-153	CH_2	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-CH_3	CH_3	$-CMe_3$	Amorphous
1-154	CH_2	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-CH_3	$-CH_2C(=O)O-Bu(t)$	$-CMe_3$	205-207
1-155	CH_2	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-CH_3	$-CO_2CH_2CH(CH_3)_2$	$-CMe_3$	Amorphous
1-156	CH_2	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-CH_3	$-CH_2CH_2CH_2Br$	$-CMe_3$	Amorphous
1-157	CH_2	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-CH_3	CN	$-CMe_3$	Amorphous
1-158	O	O	H	H	H	H	CH_3	CHO	H	H	3'-CH_3	5'-CH_3	H	$-CMe_3$	221-223
1-159	O	NH	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-CH_3	H	$-CMe_3$	
1-160	O	O	H	H	H	H	$-OCH_2OEt$	H	H	H	3'-CH_3	5'-CH_3	H	$-CMe_3$	121.5-122.5
1-161	O	O	H	H	H	H	OH	H	H	H	3'-CH_3	5'-CH_3	H	$-CMe_3$	182-184
1-162	O	O	H	H	H	H	CH_3	H	I	H	3'-CH_3	5'-CH_3	H	$-CMe_3$	
1-163	CH_2	O	H	H	H	H	CH_3	H	H	H	3'-CH_3	5'-CH_3	$-CH_2OC_2H_5$	$-CMe_3$	Amorphous

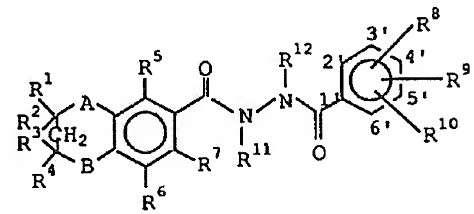


Table 14

No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
2-1	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CMe_3$	113-118
2-2	O	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	$-CH(CMe_3)Me_3$	164-165

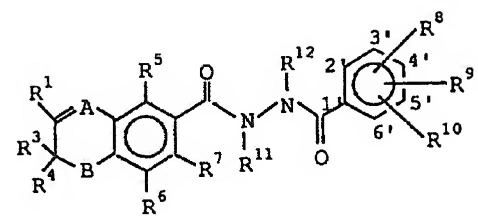


Table 15

No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
3-1	=CH-	O	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	CMe_3	183-188

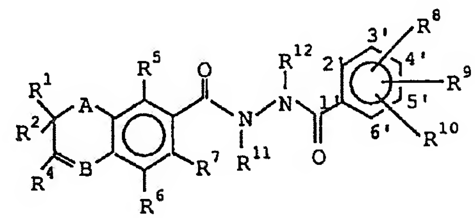


Table 16

No.	A	B	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R^{12}	Melting Point (°C)
4-1	O	=CH-	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	CMe_3	108-110
4-2	O	=CH-	Me	Me	H	H	Me	H	H	H	3'-Me	5'-Me	H	CMe_3	138-139
4-3	O	=CMe-	H	H	H	H	Me	H	H	H	3'-Me	5'-Me	H	CMe_3	

Next, the pesticidal composition is explained specifically by referring to the formulation examples.

Formulation Example 1: Emulsifiable Concentrate

To 20 parts of the compound of Compound No. 1-1 was added 65 parts of a mixed solution of xylene and methylnaphthalene, and then 15 parts of a mixture of an alkylphenol-ethylene oxide condensate and calcium alkylbenzenesulfonate (8 : 2) was mixed thereto to obtain an emulsifiable concentrate. This formulation is used as a spray solution by diluting it with water.

Formulation Example 2: Wettable Powder

To 20 parts of the compound of Compound No. 1-1, were added 35 parts of kaolin, 30 parts of clay, 7.5 parts of diatomaceous earth, and then 7.5 parts of a mixture of sodium laurate and sodium dinaphthylmethanesulfonate (1 : 1) was mixed thereto. The mixture was finely pulverized to obtain a wettable powder. This formulation is used as a spreading solution by diluting with water.

Formulation Example 3: Dust

To 1 part of the compound of Compound No. 1-8, was added 97 parts of a mixture of talc and calcium carbonate (1 : 1) and the mixture was pulverized and sufficiently and uniformly dispersed. Further, 2 parts of anhydrous silicic acid was added, and the mixture was well mixed and pulverized to obtain powder. This powder is used by spray as it is.

Formulation Example 4: Granules

To 2 parts of the compound of Compound No. 1-8, were mixed 48 parts of bentonite fine powder, 48 parts of talc and 2 parts of sodium lignin sulfonate, and then water was added thereto and the mixture was kneaded until it became uniform. Next, the mixture was granulated through an injection molding machine, and passing through a grain uniforming machine and a dryer sieve to prepare a granule having a grain size of 0.6 to 1 mm. This formulation is used by topdressing directly to paddy field surface and soil surface.

Formulation Example 5: Oil

To 0.1 part of the compound of Compound No. 1-1, was added 0.5 part of piperonyl butoxide, and kerosine was added thereto so that the total weight became 100 parts to obtain an oil. This preparation is used as it is.

Formulation Example 6: Water based Flowables

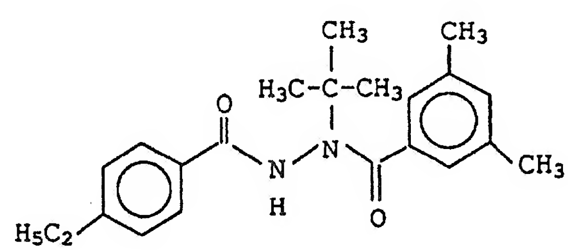
5 parts of the compound of compound No. 1-8 were mixed with 5 parts of Newkalgen (dispersing agent, Takemoto Oil & Fat Co., Ltd.), 0.2 parts of Antifoam 422 (anti-foaming agent, Rhone-Poulenc) and 74.6 parts of distilled water. Then the mixture was milled for 45 minutes at 1,000 rpm. After milling the mixture, 8 parts of propylene glycol, 2 parts of xanthan gum and 7 parts of 1% Proxcel GXL solution were added and mixed.

This formulation (5% water based flowables) is used as a spray solution by diluting it with water.

Next, the pesticidal effects of the hydrazine derivative represented by the formula (I) of the present invention will be specifically described by referring to the following Test Examples.

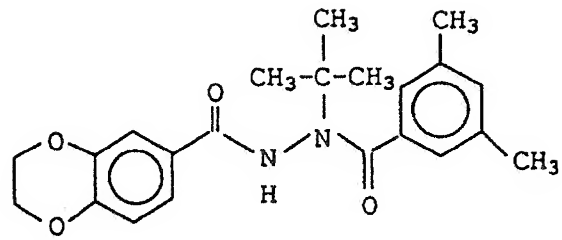
As the comparative compounds, the following compounds were used.

A:



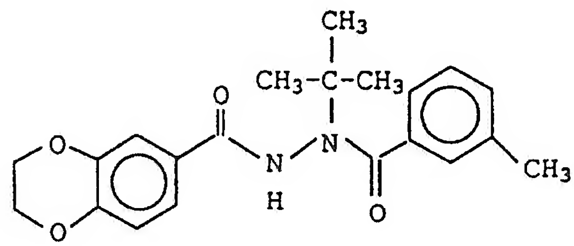
(No.200 of Japanese Patent Application Laid-Open (KOKAI) No. 62-167747 (1987))

B:



(No.10 of Japanese Patent Application Laid-Open (KOKAI) No. 3-141245 (1991))

C:



(No.9 of Japanese Patent Application Laid-Open (KOKAI) No. 3-141245 (1991))

Test Example 1: Effect to *Plutella xylostella* (foliar dipping method)

According to Formulation Examples 1 and 2, 20% wettable powder or 5% emulsifiable concentrate of the hydrazine derivative according to the present invention was prepared to obtain a test formulation. As a control formulation, prothiophos 50% emulsifiable concentrate and cypermeslin 6% emulsifiable concentrate were used.

Test method:

A cabbage leaf of a medium size cut from cabbage grown to decafoliate stage was dipped for 20 seconds in a treatment solution prepared by diluting each of the formulations with water to an effective ingredient concentration of 12.5 ppm. After air-dried, the thus treated leaf was placed in a plastic container having a diameter of 9 cm, and ten Plutella xylostella larvae (third instar) were transferred thereon. With covering by a lid having five or six pin holes, the container was left in a temperature-controlled chamber at 25°C. After 4 days from the treatment, the number of live and dead insects were counted to calculate the mortality. The results shown in Table 17 are averages of two replications. Plutella xylostella of susceptible strain (collected in Ageo) and of resistant strain (collected in Kagoshima) to organophosphorus pesticides, carbamate pesticides, pyrethroids, etc. were used.

Table 17

	Mortality (%)	
Test compound	Susceptible strain (in Ageo)	Resistant strain (in Kagoshima)
1 - 2	100	100
1 - 5	100	100
1 - 24	100	100
1 - 25	100	100
1 - 87	100	100
1 - 90	80	70
1 - 136	100	100
1 - 138	100	100

Table 17 (continued)

	Mortality (%)	
Test compound	Susceptible strain (in Ageo)	Resistant strain (in Kagoshima)
1 - 143	100	100
A	80	70
B	50	40
C	40	40
Prothiophos 200 ppm	100	0
Agroslin 60 ppm	100	0

Test Example 2: Effect to *Spodoptera litura*

According to Formulation Examples 1 and 2, 20 % wettable powder or 5 % emulsifiable concentrate of the hydrazine derivative according to the present invention was prepared and tested.

Test method:

A cabbage leaf of a medium size cut from cabbage grown to decafoliate stage was dipped for 20 seconds in a treatment solution prepared by diluting each of the formulations with water to an effective ingredient concentration of 3 ppm. After air-dried, the thus treated two leaves were placed in a plastic container having a diameter of 9 cm, and five *Spodoptera litura* larvae (third instar) were transferred thereon. With covering by a lid having five or six pin holes, he container was left in a temperature-controlled chamber at 25°C. After 4 days from the treatment, the number of live and dead insects were counted to calculate the mortality. The results shown in Table 18 are averages of two replications.

Table 18

Test compound	Mortality (%)
1 - 1	100
1 - 2	100
1 - 3	70
1 - 5	100
1 - 8	90
1 - 13	100
1 - 15	100
1 - 19	100
1 - 21	100
1 - 23	100
1 - 24	100
1 - 25	90
1 - 29	90
1 - 34	100
1 - 40	100
1 - 42	100
1 - 46	100
1 - 87	100
1 - 90	100

Table 18 (continued)

Test compound	Mortality (%)
1 - 91	100
1 - 92	100

Test compound	Mortality (%)
1 - 93	80
1 - 95	100
1 - 99	80
1 - 102	90
1 - 111	70
1 - 117	100
1 - 118	100
1 - 122	80
1 - 135	100
1 - 136	100
1 - 138	100
1 - 157	100
A	70
B	30
C	20

Test Example 3: Effect to *Cnaphalocrocis medinalis*

According to Formulation Examples 1 and 2, 20 % wettable powder or 5 % emulsifiable concentrate of the hydrazine derivative according to the present invention was prepared and tested.

Test method:

In a treatment solution prepared by diluting each of the formulations with water to an effective ingredient concentration of 1 ppm, ten rice plants of in the trifoliate were dipped for 20 seconds. After air-dried, the rice plants were wound with a urethane and fixed in a glass . cylinder (inner diameter 44 mm, height 140 mm), and five *Cnaphalocrocis medinalis* larvae (third instar) were transferred into the cylinder. After covered with a paper used for wrapping powdered medicine, the cylinder was kept still at 25°C in a temperature-controlled chamber of 16-hour diurnal. After 5 days after the treatment, the number of live and dead insects were counted to calculate the mortality. The test was carried out in two replications and susceptible strain of *Cnaphalocrocis medinalis* was tested. The results are shown in Table 19.

Table 19

Test compound	Mortality (%)
1 - 2	90
1 - 12	100
1 - 15	100
1 - 39	100
1 - 40	100
1 - 46	100

Table 19 (continued)

Test compound	Mortality (%)
1 - 48	100
1 - 50	100
1 - 87	100
1 - 138	100
1 - 157	100
A	80
B	0
C	0

Test Example 4: Effect to *Adoxophyes orana*

According to Formulation Examples 1 and 2, 20 % wettable powder or 5 % emulsifiable concentrate of the hydrazine derivative according to the present invention was prepared and tested.

Test method:

Seven green tea leaves with a length of about 5 cm were dipped for 20 seconds in a treatment solution prepared by diluting each of the formulations with water to an effective ingredient concentration of 3 ppm. After air-dried, the thus treated leaves were placed in a plastic container (inner diameter 70 mm, height 40 mm), and five *Adoxophyes orana* larvae (third instar) were transferred thereinto. The container was covered with a lid having 5 to 6 pin holes and allowed to stand at 25°C in a temperature-controlled chamber of 16-hour diurnal. After 5 days from the treatment, the number of live and dead insects were counted to calculate the mortality. The test was carried out in two replications and susceptible strain of *Adoxophyes orana* was tested. The results are shown in Table 20.

Table 20

Test compound	Mortality (%)
1 - 2	100
1 - 8	90
1 - 13	100
1 - 15	100
1 - 21	50
1 - 23	100
1 - 24	100
1 - 40	100
1 - 87	60
1 - 136	100
1 - 138	60
A	40
B	30
C	20

Test Example 5: Effect to *Plutella xylostella* (root dipping method)

According to Formulation Examples 1 and 2, 20 % wettable powder or 5 % emulsifiable concentrate of the hydrazine derivative according to the present invention was prepared and tested.

Test method:

White radish sprout of which cotyledon was opened were pulled out from soil and after washing with water, the root thereof was dipped for 2 days in a treatment solution prepared by diluting each of the formulations with water to an effective ingredient concentration of 20 ppm. The white radish sprout thus treated was placed in a glass cylinder having a diameter of 5 cm and a height of 15 cm, and *Plutella xylostella* larvae (third instar) were transferred thereinto. After the glass cylinder was covered with a paper used for wrapping powdered medicine, the cylinder was allowed to stand in a temperature-controlled chamber at 25°C. After 3 days from the treatment, the number of live and dead insects were counted to calculate the mortality. The test was carried out in two replications each containing five larvae and an average value of the mortalities were shown in Table 21. The susceptible strain of *Plutella xylostella* (collected in Ageo) were tested.

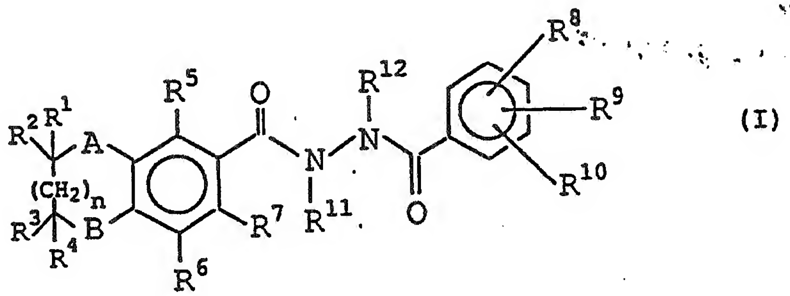
Table 21

Test compound	Mortality (%)
1 - 5	100
1 - 6	90
1 - 7	100
1 - 9	90
1 - 11	60
1 - 19	100
1 - 23	100
1 - 24	80
1 - 25	100
1 - 27	80
1 - 43	80
1 - 44	70
1 - 51	90
1 - 57	100
1 - 59	100
1 - 95	100
1 - 116	100
1 - 120	100
1 - 143	100
1 - 144	100
2 - 2	100
A	0
B	0
C	0

Claims

Claims for the following Contracting States : AT, BE, CH, DE, DK, FR, GB, GR, IT, LI, LU, NL, SE

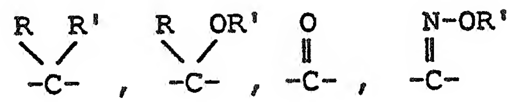
1. A hydrazine derivative represented by the following formula (I):



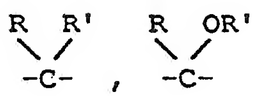
(I)

wherein

A and B each independently represent -O-, -S-,



or NR' wherein R represents a hydrogen atom, $(C_1\text{-}C_4)$alkyl group or $(C_1\text{-}C_4)$alkoxy group, R' represents a hydrogen atom, $(C_1\text{-}C_4)$alkyl group, $(C_2\text{-}C_4)$acyl group or p-fluorobenzyl group, or R and R' may be combined to form an dioxolan ring together with the carbon atom to which R and R' are attached, A or B optionally forming a double bond with an adjacent carbon atom when A and B each independently represent



or NR';

R^1, R^2, R^3 and R^4 each independently represent hydrogen atom, $(C_1\text{-}C_4)$alkyl group, $(C_1\text{-}C_4)$alkoxy$(C_1\text{-}C_4)$alkyl group or benzyloxy$(C_1\text{-}C_4)$alkyl group;

R^5, R^6 and R^7 each independently represent hydrogen atom, halogen atom, $(C_1\text{-}C_4)$alkyl group, nitro group, amino group, cyano group, hydroxyl group, formyl group, $(C_1\text{-}C_4)$haloalkyl group, $(C_2\text{-}C_4)$alkenyl group, $(C_1\text{-}C_4)$alkoxy group, $(C_1\text{-}C_4)$alkoxy$(C_1\text{-}C_4)$alkyl group, $(C_1\text{-}C_4)$alkylthio$(C_1\text{-}C_4)$alkyl group or $(C_1\text{-}C_4)$alkoxy$(C_1\text{-}C_4)$alkoxy group;

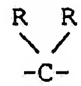
R^8, R^9 and R^{10} each independently represent hydrogen atom, halogen atom, $(C_1\text{-}C_4)$alkyl group, tri$(C_1\text{-}C_4)$alkylsilyloxy$(C_1\text{-}C_4)$alkyl group, nitro group, $(C_1\text{-}C_4)$haloalkyl group, hydroxy$(C_1\text{-}C_4)$alkyl group, formyl group, $(C_1\text{-}C_4)$alkoxy group, $(C_2\text{-}6_4)$alkenyloxy group, $(C_2\text{-}C_4)$alkynyloxy group, $(C_2\text{-}C_4)$alkenyl group, $(C_2\text{-}C_4)$alkynyl group, $(C_1\text{-}C_4)$haloalkoxy group, $(C_1\text{-}C_4)$haloalkylthio group, $(C_1\text{-}C_4)$alkoxy$(C_1\text{-}C_4)$alkoxy group, $(C_1\text{-}C_4)$alkoxy group having a phenyl group which is optionally substituted by a halogen atom, or $(C_1\text{-}C_4)$alkoxy group having a phenoxy group which is optionally substituted by a CF_3, halogen atom or $(C_1\text{-}C_2)$alkyl group;

R^{11} represents a hydrogen atom, cyano group, $(C_1\text{-}C_4)$haloalkylthio group, $(C_2\text{-}C_5)$acyl group, di$(C_1\text{-}C_4)$alkylcarbamoyl group, $(C_1\text{-}C_4)$alkoxycarbonyl group, $(C_1\text{-}C_4)$alkoxycarbonylcarbonyl group, $(C_2\text{-}C_4)$alkenyl group or $(C_1\text{-}C_4)$alkyl group which is optionally substituted by a halogen atom, $(C_1\text{-}C_4)$alkoxy group, $(C_1\text{-}C_6)$alkylcarbonyloxy group or $(C_1\text{-}C_4)$alkoxycarbonyl group;

R^{12} represents a branched $(C_3\text{-}C_{10})$alkyl group; and

n represents 0 or 1;

with the proviso that when A and B each independently represent -O- or



wherein R and R' each independently represent a hydrogen atom or $(C_1\text{-}C_4)$alkyl group, at least one of R^5, R^6 and R^7 is not a hydrogen atom.

2. A hydrazine derivative according to Claim 1, wherein

A represents -O- or $-CH_2-$;
B represents -O- or $-CH_2-$;
R^1, R^2, R^3 and R^4 each independently represent a hydrogen atom or a methyl group;
R^5 represents a $(C_1\text{-}C_4)$alkyl group, a $(C_1\text{-}C_4)$haloalkyl group or a halogen atom;
R^6 represents a hydrogen atom, a $(C_1\text{-}C_4)$alkyl group or a halogen atom;
R^7 represents a hydrogen atom or a halogen atom;
R^8, R^9 and R^{10} each independently represents a hydrogen atom, a $(C_1\text{-}C_4)$alkyl group, a $(C_1\text{-}C_4)$haloalkyl group, a halogen atom, a nitro group, a $(C_1\text{-}C_4)$alkoxy group, a $(C_2\text{-}C_4)$alkenyloxy group, a $(C_2\text{-}C_4)$alkynyloxy group, a $(C_2\text{-}C_4)$alkenyl group, a $(C_1\text{-}C_4)$haloalkoxy group, a phenyl$(C_1\text{-}C_4)$alkoxy group whose phenyl moiety is optionally substituted with a halogen atom, or a phenoxy$(C_1\text{-}C_4)$alkoxy group whose phenyl moiety is optionally substituted with a $(C_1\text{-}C_2)$alkyl group, CF_3 or halogen atom;
R^{11} represents a hydrogen atom, a cyano group, a $(C_1\text{-}C_4)$haloalkylthio group, a $(C_1\text{-}C_4)$alkoxycarbonylcarbonyl group or a $(C_1\text{-}C_4)$alkylcarbonyloxymethyl group;
R^{12} represents a branched $(C_4\text{-}C_8)$alkyl group; and
n represents 0.

3. A hydrazine derivative according to claim 1, wherein

A represents -O- or $-CH_2-$;
B represents -O-;
R^1, R^2, R^3 and R^4 each represents a hydrogen atom;
R^5 represents a $(C_1\text{-}C_2)$alkyl group, a $(C_1\text{-}C_2)$haloalkyl group or a halogen atom;
R^6 represents a hydrogen atom;
R^7 represents a hydrogen atom;
R^8, R^9 and R^{10} each independently represents a hydrogen atom, a $(C_1\text{-}C_2)$alkyl group, a $(C_1\text{-}C_2)$haloalkyl group, a halogen atom, a nitro group or a $(C_1\text{-}C_2)$alkoxy group;
R^{11} represents a hydrogen atom, a cyano group, a trichloromethylthio group, an ethoxycarbonylcarbonyl group or a pivaloyloxymethyl group;
R^{12} represents a branched $(C_4\text{-}C_6)$alkyl group; and
n represents 0.

4. A hydrazine derivative according to claim 1, wherein

A represents -O- or $-CH_2-$;
B represents -O-;
R^1, R^2, R^3 and R^4 each represents a hydrogen atom;
R^5 represents a $(C_1\text{-}C_2)$alkyl group;
R^6 represents a hydrogen atom;
R^7 represents a hydrogen atom;
R^8, R^9 and R^{10} each independently represents a hydrogen atom, a methyl group, a mono-, di- or trifluoromethyl group, a chlorine atom, a fluorine atom, a nitro group or a methoxy group;
R^{11} represents a hydrogen atom, a cyano group, a trichloromethylthio group, an ethoxycarbonylcarbonyl group or a pivaloyloxymethyl group;
R^{12} represents a branched $(C_4\text{-}C_6)$alkyl group; and
n represents 0.

5. A hydrazine derivative according to claim 1, wherein

A represents -O- or $-CH_2-$;
B represents -O-;
R^1, R^2, R^3 and R^4 each represents a hydrogen atom;
R^5 represents a (C_1-C_2)alkyl group;
R^6 represents a hydrogen atom;
R^7 represents a hydrogen atom;
R^8, R^9 and R^{10}, together with the phenyl group to which they are attached, represent a 3,5-dimethylphenyl group, a 3,5-dichlorophenyl group, a 2,4-dichlorophenyl group, a 3-fluoromethyl-5-methylphenyl group, a 3-difluoromethyl-5-methylphenyl group or a 3,5-dimethyl-4-fluorophenyl group;
R^{11} represents a hydrogen atom, a cyano group or a trichloromethylthio group;
R^{12} represents a t-butyl group, a 2,2-dimethylpropyl group or a 1,2,2-trimethylpropyl group; and
n represents 0.

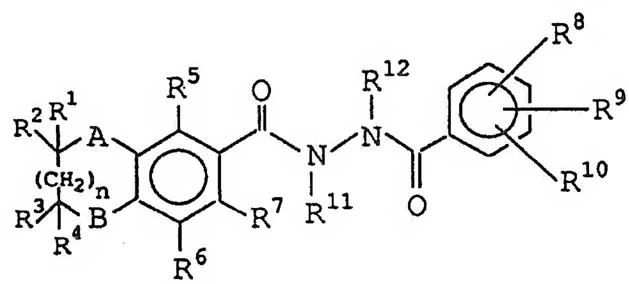
6. A hydrazine derivative according to claim 1, which is selected from the group consisting of:

N-(5-methylchroman-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazine,
N-cyano-N-(5-methylchroman-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazine,
N-(5-methylchroman-6-carbo)-N'-t-butyl-N'-(3,5-dimethyl-4-fluorobenzoyl)hydrazine,
N-(5-methylchroman-6-carbo)-N-trichloromethylthio-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazine,
N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-(2,2-dimethylpropyl)-N'-(3,5-dimethylbenzoyl)hydrazine,
N-cyano-N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazine,
N-(5-methyl-1,4-benzodioxan-6-carbo)-N-trichloromethylthio-N'-t-butyl-N'-(3,5-dimethylbenzoyl)-hydrazine,
N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-dichlorobenzoyl)hydrazine,
N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3-difluoromethyl-5-methylbenzoyl)hydrazine,
N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-(1,2,2-trimethylpropyl)-N'-(3,5-dimethylbenzoyl)hydrazine, and
N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazine.

7. A pesticidal composition which comprises a pesticidally effective amount of the hydrazine derivative as defined in any of Claims 1 to 6 as an effective ingredient and a pesticidally acceptable adjuvant.

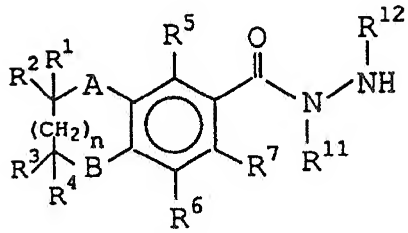
8. A method for controlling a harmful pest which comprises applying the hydrazine derivative as defined in any of Claims 1 to 6 to the harmful pest.

9. A process for producing a hydrazine derivative represented by the formula (I):



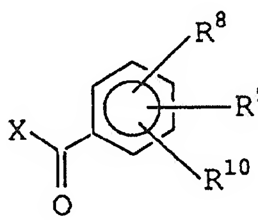
(I)

wherein R^1 to R^{12}, A, B and n are as defined in Claim 1, which comprises reacting a hydrazide represented by the formula (II):



(II)

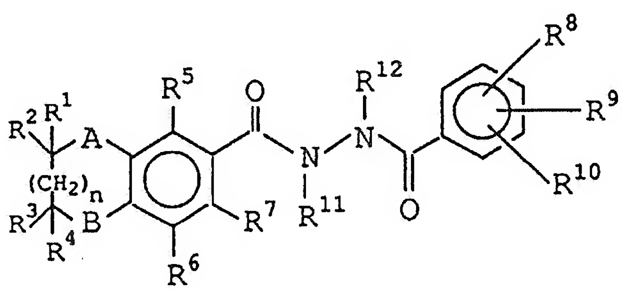
wherein R^1 to R^7, R^{11}, R^{12}, A, B and n are as defined in Claim 1, with a benzoyl halide represented by the formula (III):



(III)

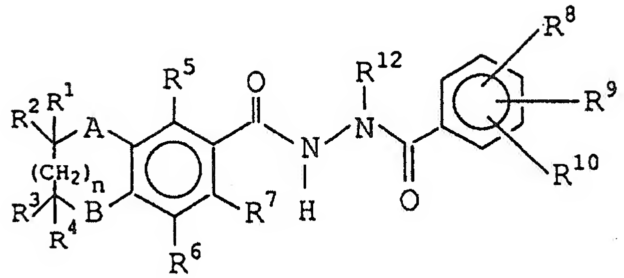
wherein X is a halogen atom, and R^8 to R^{10} are as defined in Claim 1, in an inert solvent in the presence of a base.

10. A process for producing a hydrazine derivative represented by the formula (I):



(I)

wherein R^1 to R^{10}, R^{12}, A, B and n are as defined in Claim 1, and R^{11} is a cyano group, (C_1-C_4)haloalkylthio group, (C_2-C_5)acyl group, di(C_1-C_4)alkylcarbamoyl group, (C_1-C_4)alkoxycarbonyl group, (C_1-C_4)alkoxycarbonylcarbonyl group, (C_1-C_4)alkyl group which is optionally substituted by a halogen atom, (C_1-C_4)alkoxy group, (C_1-C_6)alkylcarbonyloxy group or (C_1-C_4)alkoxycarbonyl group, or (C_2-C_4)alkenyl group, which comprises reacting a hydrazine derivative represented by the formula (Ia):



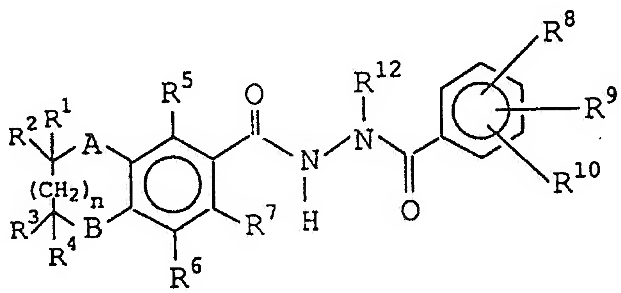
(Ia)

wherein R^1 to R^{10}, R^{12}, A, B and n are as defined in Claim 1, with a halide represented by the formula (IIa):

$$X\text{-}R^{11} \quad \text{(IIA)}$$

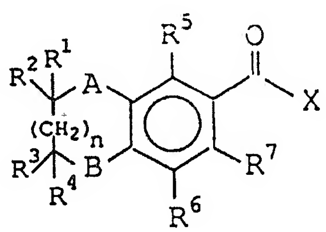
wherein X is a halogen atom and R^{11} is defined as above, in an inert solvent in the presence of a base.

11. A process for producing a hydrazine derivative represented by the formula (Ia):



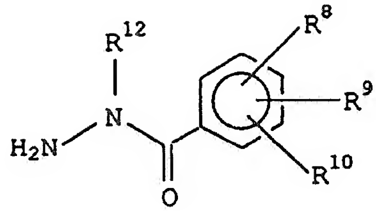
(Ia)

wherein R^1 to R^{10}, R^{12}, A, B and n are as defined in Claim 1, which comprises reacting a benzoyl halide represented by the formula (IV):



(IV)

wherein R^1 to R^7, A, B, and n are as defined in Claim 1, and X is a halogen atom, with a hydrazide represented by the formula (IX):

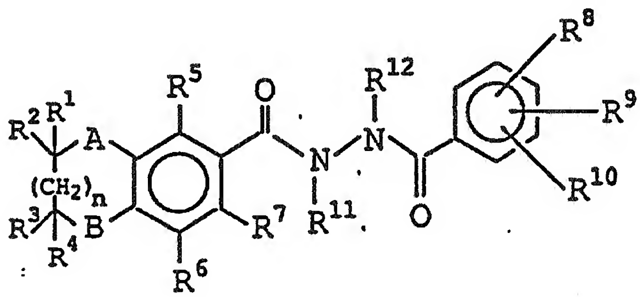


(IX)

wherein R^8 to R^{10} and R^{12} are as defined in Claim 1, in an inert solvent in the presence of a base.

Claims for the following Contracting State : ES

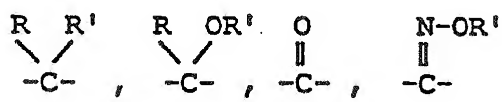
1. A process for producing a hydrazine derivative represented by the following formula (I):



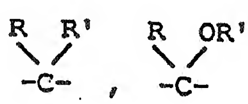
(I)

wherein

A and B each independently represent -O-, -S-,



or NR' wherein R represents a hydrogen atom, $(C_1\text{-}C_4)$alkyl group or $(C_1\text{-}C_4)$alkoxy group, R' represents a hydrogen atom, $(C_1\text{-}C_4)$alkyl group, $(C_2\text{-}C_4)$acyl group or p-fluorobenzyl group, or R and R' may be combined to form an dioxolan ring together with the carbon atom to which R and R' are attached, A or B optionally forming a double bond with an adjacent carbon atom when A and B each independently represent



or NR';

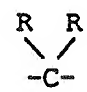
R^1, R^2, R^3 and R^4 each independently represent hydrogen atom, $(C_1\text{-}C_4)$alkyl group, $(C_1\text{-}C_4)$alkoxy$(C_1\text{-}C_4)$ alkyl group or benzyloxy$(C_1\text{-}C_4)$alkyl group;

R^5, R^6 and R^7 each independently represent hydrogen atom, halogen atom, $(C_1\text{-}C_4)$alkyl group, nitro group, amino group, cyano group, hydroxyl group, formyl group, $(C_1\text{-}C_4)$haloalkyl group, $(C_2\text{-}C_4)$alkenyl group, $(C_1\text{-}C_4)$alkoxy group, $(C_1\text{-}C_4)$ alkoxy $(C_1\text{-}C_4)$ alkyl group, $(C_1\text{-}C_4)$ alkylthio $(C_1\text{-}C_4)$alkyl group or $(C_1\text{-}C_4)$alkoxy$(C_1\text{-}C_4)$alkoxy group;

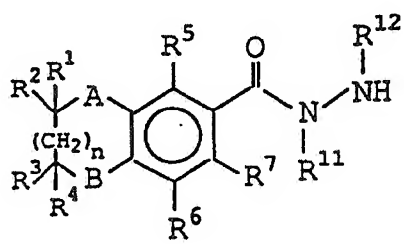
R^8, R^9 and R^{10} each independently represent hydrogen atom, halogen atom, $(C_1\text{-}C_4)$alkyl group, tri$(C_1\text{-}C_4)$ alkylsilyloxy$(C_1\text{-}C_4)$alkyl group, nitro group, $(C_1\text{-}C_4)$haloalkyl group, hydroxy$(C_1\text{-}C_4)$alkyl group, formyl group,

(C_1-C_4)alkoxy group, (C_2-C_4)alkenyloxy group, (C_2-C_4)alkynyloxy group, (C_2-C_4)alkenyl group, (C_2-C_4)alkynyl group, (C_1-C_4)haloalkoxy group, (C_1-C_4)haloalkylthio group, (C_1-C_4) alkoxy (C_1-C_4) alkoxy group, (C_1-C_4) alkoxy group having a phenyl group which is optionally substituted by a halogen atom, or (C_1-C_4)alkoxy group having a phenoxy group which is optionally substituted by a CF_3, halogen atom or (C_1-C_2)alkyl group;
R^{11} represents a hydrogen atom, cyano group, (C_1-C_4)haloalkylthio group, (C_2-C_5)acyl group, di(C_1-C_4)alkyl-carbamoyl group, (C_1-C_4)alkoxycarbonyl group, (C_1-C_4) alkoxycarbonylcarbonyl group, (C_2-C_4)alkenyl group or (C_1-C_4)alkyl group which is optionally substituted by a halogen atom, (C_1-C_4)alkoxy group, (C_1-C_6) alkyl-carbonyloxy group or (C_1-C_4)alkoxycarbonyl group;
R^{12} represents a branched (C_3-C_{10})alkyl group; and
n represents 0 or 1;

with the proviso that when A and B each independently represent -O- or

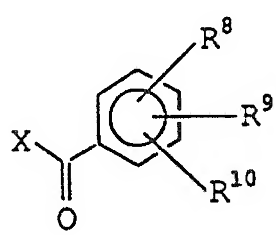


wherein R and R' each independently represent a hydrogen atom or (C_1-C_4)alkyl group, at least one of R^5, R^6 and R^7 is not a hydrogen atom,
which comprises reacting a hydrazide represented by the formula (II):



(II)

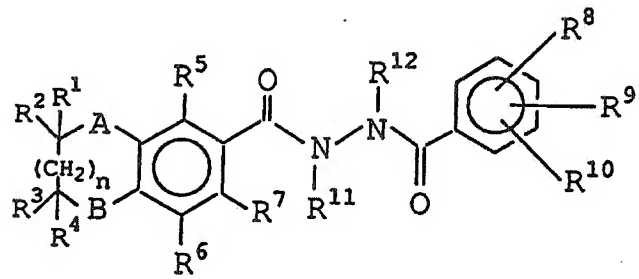
wherein R^1 to R^7, R^{11}, R^{12}, A, B and n are as defined above,
with a benzoyl halide represented by the formula (III):



(III)

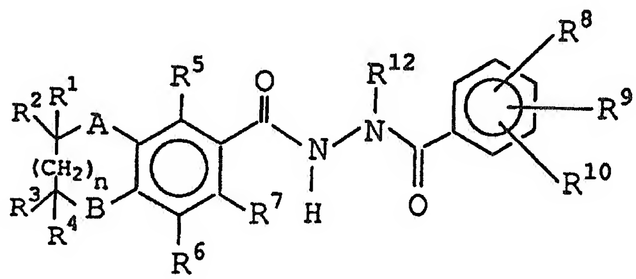
wherein X is a halogen atom, and R^8 to R^{10} are as defined above,
in an inert solvent in the presence of a base.

2. A process for producing a hydrazine derivative represented by the formula (I):



(I)

wherein R^1 to R^{10}, R^{12}, A, B and n are as defined in Claim 1, and R^{11} is a cyano group, $(C_1$-$C_4)$haloalkylthio group, $(C_2$-$C_5)$acyl group, di$(C_1$-$C_4)$alkylcarbamoyl group, $(C_1$-$C_4)$ alkoxycarbonyl group, $(C_1$-$C_4)$alkoxycarbonylcarbonyl group, $(C_1$-$C_4)$alkyl group which is optionally substituted by a halogen atom, $(C_1$-$C_4)$alkoxy group, $(C_1$-$C_6)$alkylcarbonyloxy group or $(C_1$-$C_4)$alkoxycarbonyl group, or $(C_2$-$C_4)$alkenyl group,
which comprises reacting a hydrazine derivative represented by the formula (Ia) :



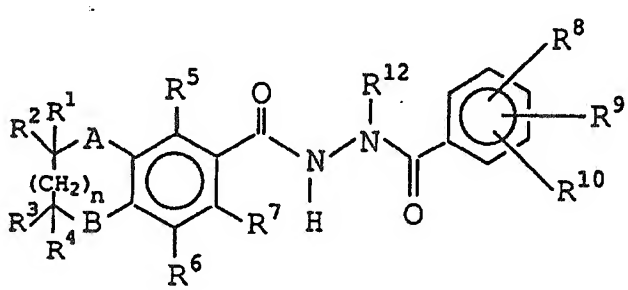
(Ia)

wherein R^1 to R^{10}, R^{12}, A, B and n are as defined in Claim 1,
with a halide represented by the formula (IIa) :

$$X\text{-}R^{11} \qquad \text{(IIa)}$$

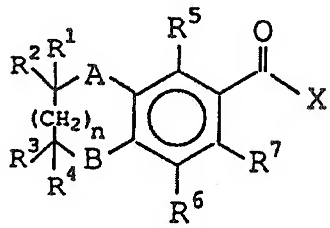
wherein X is a halogen atom and R^{11} is defined as above, in an inert solvent in the presence of a base.

3. A process for producing a hydrazine derivative represented by the formula (Ia):



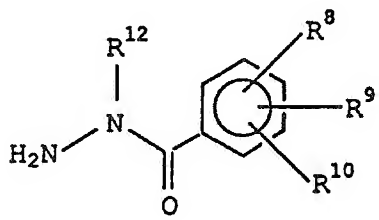
(Ia)

wherein R^1 to R^{10}, R^{12}, A, B and n are as defined in Claim 1,
which comprises reacting a benzoyl halide represented by the formula (IV) :



(IV)

wherein R^1 to R^7, A, B, and n are as defined in Claim 1, and X is a halogen atom, with a hydrazide represented by the formula (IX):



(IX)

wherein R^8 to R^{10} and R^{12} are as defined in Claim 1, in an inert solvent in the presence of a base.

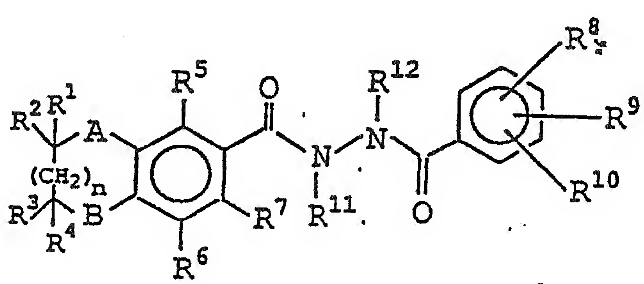
4. Modification of the process of claims 1 to 3, additionally comprising admixture or presentation of the compound obtained according to one or more of claims 1 to 3 with a pesticidally acceptable, adjuvant and, optionally, other pesticidally active substances and/or synergists.

5. Pesticidal composition, which comprises 0.02 to 95% by weight of a compound obtained according to one or more of claims 1 to 3 and a pesticidally acceptable adjuvant and, optionally, other pesticidally active substances and/or synergists.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : AT, BE, CH, DE, DK, FR, GB, GR, IT, LI, LU, NL, SE

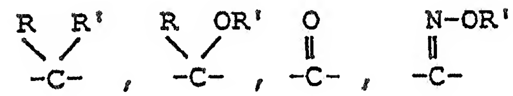
1. Ein durch die folgende Formel (I) dargestelltes Hydrazinderivat



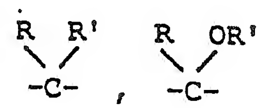
(I)

wobei

A und B jeweils unabhängig -O-, -S-,



oder NR' darstellen, wobei R ein Wasserstoffatom, (C_1-C_4)Alkylgruppe oder (C_1-C_4)Alkoxygruppe darstellt, R' ein Wasserstoffatom, (C_1-C_4)Alkylgruppe, (C_2-C_4)Acylgruppe oder p-Fluorbenzylgruppe darstellt, oder R und R' gemeinsam mit den Kohlenstoffatomen, an die R und R' gebunden sind, unter Bildung eines Dioxolanrings verbunden sein können wobei A oder B gegebenenfalls eine Doppelbindung mit dem benachbarten Kohlenstoffatom bilden können, wenn A und B jeweils unabhängig



oder NR';

R^1, R^2, R^3 und R^4 jeweils unabhängig Wasserstoffatom, (C_1-C_4)Alkylgruppe, (C_1-C_4)Alkoxy(C_1-C_4)alkylgruppe oder Benzyloxy(C_1-C_4)alkylgruppe darstellen;

R^5, R^6 und R^7 jeweils unabhängig Wasserstoffatom, Halogenatom (C_1-C_4)Alkylgruppe, Nitrogruppe, Aminogruppe, Cyanogruppe, Hydroxylgruppe, Formylgruppe, (C_1-C_4)Haloalkylgruppe, (C_2-C_4)Alkenylgruppe, (C_1-C_4)Alkoxygruppe, (C_1-C_4)Alkoxy(C_1-C_4)alkylgruppe, (C_1-C_4)Alkylthio(C_1-C_4)alkylgruppe oder (C_1-C_4)Alkoxy (C_1-C_4)alkoxygruppe darstellen;

R^8, R^9 und R^{10} jeweils unabhängig Wasserstoffatom, Halogenatom, (C_1-C_4)Alkylgruppe, Tri(C_1-C_4)alkylsilyloxy(C_1-C_4)alkylgruppe, Nitrogruppe, (C_1-C_4)Haloalkylgruppe, Hydroxy(C_1-C_4)alkylgruppe, Formylgruppe, (C_1-C_4)Alkoxygruppe, (C_2-C_4)Alkenyloxygruppe, (C_2-C_4)Alkinyloxygruppe, (C_1-C_4)Haloalkoxygruppe, (C_1-C_4)Haloalkylthiogruppe, (C_1-C_4)Alkoxy(C_1-C_4)alkoxygruppe, (C_1-C_4)Alkoxygruppe mit einer Phenylgruppe, die gegebenenfalls durch ein Halogenatom substituiert ist, oder (C_1-C_4)Alkoxygruppe mit einer Phenoxygruppe, die gegebenenfalls durch CF_3, Halogenatom oder (C_1-C_2)Alkylgruppe substituiert ist, darstellen;

R^{11} ein Wasserstoffatom, Cyanogruppe, (C_1-C_4)Haloalkylthiogruppe, (C_2-C_5)Acylgruppe, Tri(C_1-C_4)alkylcarbomoylgruppe, (C_1-C_4)Alkoxycarbonylgruppe, (C_1-C_4)Alkoxycarbonylgruppe, (C_2-C_4)Alkenylgruppe oder (C_1-C_4)Alkylgruppe, die gegebenenfalls durch ein Halogenatom, (C_1-C_4)Alkoxygruppe, (C_1-C_6)Alkylcarbonyloxygruppe oder (C_1-C_4)Alkoxycarbonylgruppe substituiert ist, darstellt;

R^{12} eine verzweigte (C_3-C_{10})-Alkylgruppe darstellt; und

n 0 oder 1 darstellt;

mit dem Vorbehalt, daß, wenn A und B jeweils unabhängig -O- oder

darstellt, wobei Rund R' jeweils unabhängig ein Wasserstoffatom oder (C_1-C_4)Alkylgruppe darstellen, mindestens einer von R^5, R^6 und R^7 kein Wasserstoffatom ist.

2. Ein Hydrazinderivat entsprechend Anspruch 1, wobei

A -O- oder $-CH_2-$ darstellt;
B -O- oder $-CH_2-$ darstellt;

R^1, R^2, R^3 und R^4 jeweils unabhängig ein Wasserstoffatom oder eine Methylgruppe darstellen;
R^5 eine $(C_1$-$C_4)$Alkylgruppe, eine $(C_1$-$C_4)$Haloalkylgruppe oder ein Halogenatom darstellen;
R^6 ein Wasserstoffatom, eine $(C_1$-$C_4)$Alkylgruppe oder ein Halogenatom darstellen;
R^7 ein Wasserstoffatom oder ein Halogenatom darstellt;
R^8, R^9 und R^{10} jeweils unabhängig ein Wasserstoffatom, eine $(C_1$-$C_4)$Alkylgruppe, eine $(C_1$-$C_4)$Haloalkylgruppe, ein Halogenatom, eine Nitrogruppe, eine $(C_1$-$C_4)$Alkoxygruppe, eine $(C_2$-$C_4)$Alkenyloxygruppe, eine $(C_2$-$C_4)$Alkinyloxygruppe, eine $(C_2$-$C_4)$Alkenylgruppe, eine $(C_1$-$C_4)$Haloalkoxygruppe, eine Phenyl$(C_1$-$C_4)$alkoxygruppe, deren Phenylgruppe gegebenenfalls mit einem Halogenatom substituiert ist, oder eine Phenoxy$(C_1$-$C_4)$alkoxygruppe, deren Phenyleinheit gegebenenfalls mit einer $(C_1$-$C_2)$Alkylgruppe, CF_3 oder Halogenatom substituiert ist, darstellen;
R^{11} ein Wasserstoffatom, eine Cyanogruppe, eine $(C_1$-$C_4)$Haloalkylthiogruppe, eine $(C_1$-$C_4)$Alkoxycarbonylcarbonylgruppe oder eine $(C_1$-$C_4)$Alkylcarbonyloxymethylgruppe darstellt;
R^{12} eine verzweigte $(C_4$-$C_8)$Alkylgruppe darstellt; und n 0 darstellt.

3. Ein Hydrazinderivat entsprechend Anspruch 1, wobei

A -O- oder $-CH_2$-darstellt;

B -O- darstellt;

R^1, R^2, R^3 und R^4 jeweils ein Wasserstoffatom darstellten;

R^5 eine $(C_1$-$C_2)$Alkylgruppe, eine $(C_1$-$C_2)$Haloalkylgruppe oder ein Halogenatom darstellt;

R^6 ein Wasserstoffatom darstellt;

R^7 ein Wasserstoffatom darstellt;

R^8, R^9 und R^{10} jeweils unabhängig ein Wasserstoffatom, eine $(C_1$-$C_2)$Alkylgruppe, eine $(C_1$-$C_2)$Haloalkylgruppe, ein Halogenatom, eine Nitrogruppe oder eine $(C_1$-$C_2)$Alkoxygruppe darstellt;

R^{11} ein Wasserstoffatom, eine Cyanogruppe, eine Trichlormethylthiogruppe, eine Ethoxycarbonylcarbonylgruppe oder eine Pivaloyloxymethylgruppe darstellt;

R^{12} eine verzweigte $(C_4$-$C_6)$Alkylgruppe darstellt;

n 0 darstellt.

4. Ein Hydrazinderivat entsprechend Anspruch 1, wobei

A -O- oder $-CH_2$-darstellt;

B -O- darstellt;

R^1, R^2, R^3 und R^4 jeweils ein Wasserstoffatom darstellt;

R^5 eine $(C_1$-$C_2)$Alkylgruppe darstellt;

R^6 ein Wasserstoffatom darstellt;

R^7 ein Wasserstoffatom darstellt;

R^8, R^9 und R^{10} jeweils unabhängig ein Wasserstoffatom, eine Methylgruppe, eine Mono-, Di- oder Trifluormethylgruppe, ein Chloratom, ein Fluoratom, eine Nitrogruppe oder eine Methoxygruppe darstellt;

R^{11} ein Wasserstoffatom, eine Cyanogruppe, eine Trichlormethylthiogruppe, eine Ethoxycarbonylcarbonylgruppe oder eine Pivaloyloxymethylgruppe darstellt;

R^{12} eine verzweigte (C_4-C_6)Alkylgruppe darstellt;

n 0 darstellt.

5. Ein Hydrazinderivat entsprechend Anspruch 1, wobei

A -0- oder $-CH_2-$darstellt;

B -0- darstellt;

R^1, R^2, R^3 und R^4 jeweils ein Wasserstoffatom darstellt;

R^5 eine (C_1-C_2)Alkylgruppe darstellt;

R^6 ein Wasserstoffatom darstellt;

R^7 ein Wasserstoffatom darstellt;

R^8, R^9 und R^{10} gemeinsam mit der Phenylgruppe, an die sie gebunden sind, eine 3,5-Dimethylphenylgruppe, eine 3,5-Dichlorphenylgruppe, eine 2,4-Dichlorphenylgruppe, eine 3-Fluormethyl-5-methylphenylgruppe, eine 3-Difluormethyl-5-methylphenylgruppe oder eine 3,5-Dimethyl -4-fluorphenylgruppe darstellen;

R^{11} ein Wasserstoffatom, eine Cyanogruppe oder eine Trichlormethylthiogruppe darstellt;

R^{12} eine t-Butylgruppe, eine 2,2-Dimethylpropylgruppe oder eine 1,2,2-Trimethylpropylgruppe darstellt; und

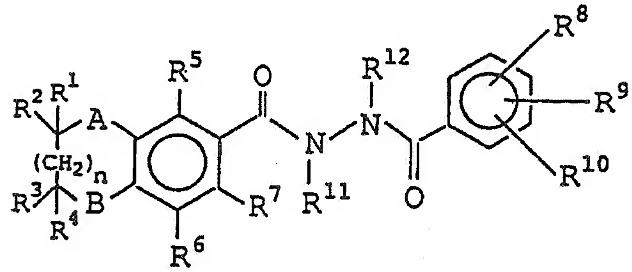
n 0 darstellt.

6. Ein Hydrazinderivat entsprechend Anspruch 1, das ausgewählt wird aus der aus: N-(5-Methylchroman-6-carbol)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazin, N-Cyano-N-(5-methylchroman-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazin, N-(5-Methylchroman-6-carbo)-N'-t-butyl-N'-(3,5-dimethyl-4-fluorbenzoyl)hydrazin, N-(5-Methylchroman-6-carbo)-N-trichlormethylthio-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazin, N-(5-Methyl-1,4-benzodioxan-6-carbo)-N'-(2,2-dimethylpropyl)-N'-(3,5-dimethylbenzoyl)hydrazin, N-Cyano-N-(5-methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazin, N-(5-Methyl-1,4-benzodioxan-6-carbo)-N-trichloimethylthio-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazin, N-(5-Methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-dichlorbenzoyl) hydrazin, N-(5-Methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3-difluormethyl-5-methylbenzoyl)hydrazin, N-(5-Methyl-1,4-benzodioxan-6-carbo)-N'-(1,2,2-trimethylpropyl)-N'-(3,5-dimethylbenzoyl)hydrazin und N-(5-Methyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-dimethylbenzoyl)hydrazin bestehenden Gruppe.

7. Eine pestizide Zusammensetzung, die eine pestizidwirksame Menge des in einem der Ansprüche 1 bis 6 definierten Hydrazinderivats als wirksamen Bestandteil und einen pestizidverträglichen Hilfsstoff enthält.

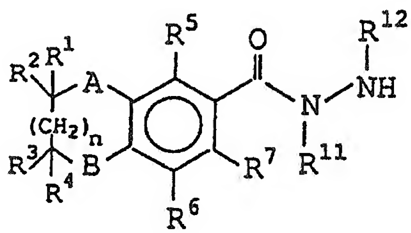
8. Eine Methode zur Kontrolle von schädlichem Ungeziefer, die Anwenden des in einem der Ansprüche 1 bis 6 definierten Hydrazinderivats bei einem schädlichen Ungeziefer umfaßt.

9. Ein Verfahren zur Herstellung eines durch Formel (I) dargestellten Hydrazinderivats:



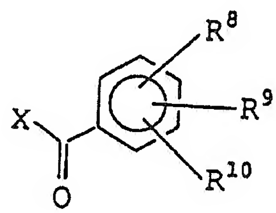
(I)

wobei R^1 bis R^{12}, A, B und n wie in Anspruch 1 definiert sind, das Umsetzen eines durch die Formel (II) dargestellten Hydrazids:



(II)

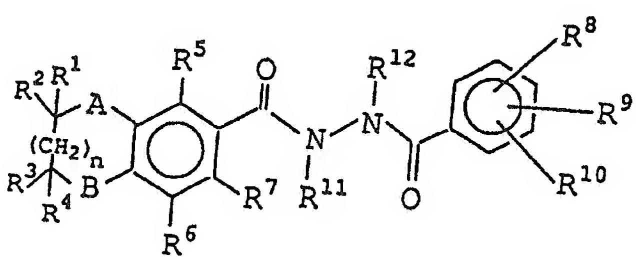
wobei R^1 bis R^7, R^{11}, R^{12}, A, B und n wie in Anspruch 1 definiert sind, mit einem durch die Formel (III) dargestellten Benzoylhalogenid:



(III)

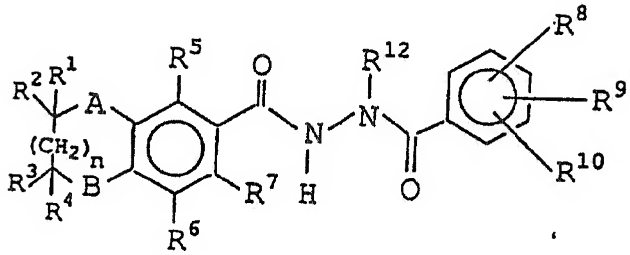
wobei X ein Halogenatom ist und R^8 bis R^{10} wie in Anspruch 1 definiert sind, in einem inerten Lösungsmittel in Gegenwart einer Base umfaßt.

10. Ein Verfahren zur Herstellung eines durch Formel (I) dargestellten Hydrazinderivats:



(I)

wobei R^1 bis R^{10}, R^{12}, A, B und n wie in Anspruch 1 definiert sind und R^{11} eine Cyanogruppe, (C_1-C_4)Haloalkylthiogruppe, (C_2-C_5)Acylgruppe, Di(C_1-C_4)alkylcarbomoylgruppe, (C_1-C_4)Alkoxycarbonylgruppe, $(C_1$-C4)Alkoxycarbonylcarbonylgruppe, (C_1-C_4)Alkylgruppe, die gegebenenfalls mit einem Halogenatom, (C_1-C_4)Alkoxygruppe, $(C_1$-C6)Alkylcarbonyloxygruppe oder (C_1-C_4)Alkoxycarbonylgruppe substituiert ist, oder (C_2-C_4)Alkenylgruppe ist,
die Reaktion eines durch die Formel (Ia) dargestellten Hydrazinderivats:



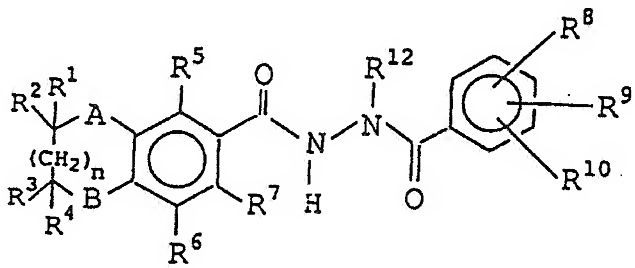
(Ia)

wobei R^1 bis R^{10}, R^{12}, A, B und n wie in Anspruch 1 definiert sind, mit einem durch die Formel (IIa) dargestellten Halogenid:

$$X\text{-}R^{11} \qquad \text{(IIa)}$$

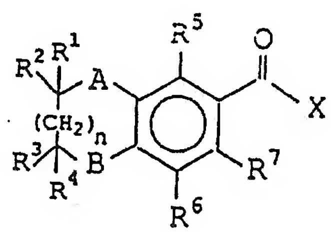
wobei X ein Halogenatom ist und R^{11} wie oben definiert ist,
in einem inerten Lösungsmittel in Gegenwart einer Base umfaßt.

11. Ein Verfahren zur Herstellung eines durch die Formel (Ia) dargestellten Hydrazinderivats:



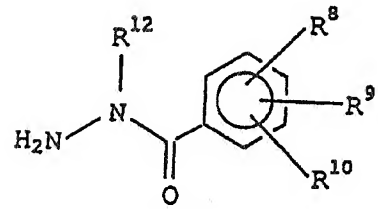
(Ia)

wobei R^1 bis R^{10}, R^{12}, A, B und n wie in Anspruch 1 definiert sind,
das Umsetzung eines durch die Formel (IV) dargestellten Benzoylhalogenids:



(IV)

wobei R^1 bis R^7, A, Bund n wie in Anspruch 1 definiert sind, und X ein Halogenatom ist,
mit einem durch die Formel (IX) dargestellten Hydrazid:

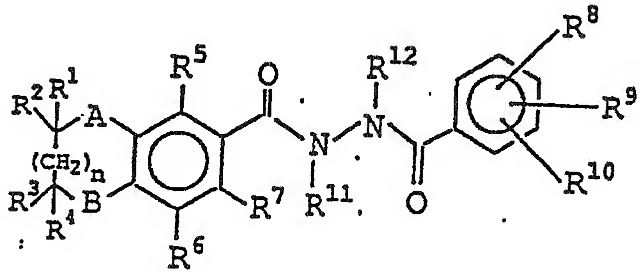


(IX)

wobei R^8 bis R^{10} und R^{12} wie in Anspruch 1 definiert sind, in einem inerten Lösungsmittel in Gegenwart einer Base umfaßt.

Patentansprüche für folgenden Vertragsstaat : ES

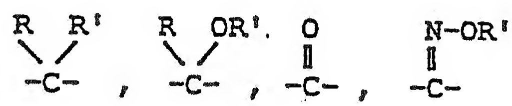
1. Ein Verfahren zur Herstellung eines durch die folgende Formel (I) dargestellten Hydrazinderivats:



(I)

wobei

A und B jeweils unabhängig -O-, -S-,



oder NR' darstellen, wobei R ein Wasserstoffatom, (C_1-C_4)Alkylgruppe oder (C_1-C_4)Alkoxygruppe darstellt, R' ein Wasserstoffatom, (C_1-C_4)Alkylgruppe, (C_2-C_4)Acylgruppe oder p-Fluorbenzylgruppe darstellt, oder R und R' gemeinsam mit den Kohlenstoffatomen, an die R und R' gebunden sind, unter Bildung eines Dioxolanrings verbunden sein können, wobei A oder B gegebenenfalls eine Doppelbindung mit dem benachbarten Kohlenstoffatom bilden können, wenn A und B jeweils unabhängig

oder NR' darstellen;

R^1, R^2, R^3 und R^4 jeweils unabhängig Wasserstoffatom, (C_1-C_4)Alkylgruppe, (C_1-C_4)Alkoxy(C_1-C_4)alkylgruppe oder Benzyloxy(C_1-C_4)alkylgruppe darstellen;

R^5, R^6 und R^7 jeweils unabhängig Wasserstoffatom, Halogenatom (C_1-C_4)Alkylgruppe, Nitrogruppe, Amino-

gruppe, Cyanogruppe, Hydroxylgruppe, Formylgruppe, $(C_1\text{-}C_4)$Haloalkylgruppe, $(C_2\text{-}C_4)$Alkenylgruppe, $(C_1\text{-}C_4)$Alkoxygruppe, $(C_1\text{-}C_4)$Alkoxy$(C_1\text{-}C_4)$alkylgruppe, $(C_1\text{-}C_4)$Alkylthio$(C_1\text{-}C_4)$alkylgruppe oder $(C_1\text{-}C_4)$Alkoxy $(C_1\text{-}C_4)$alkoxygruppe darstellen;

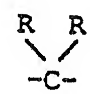
R^8, R^9 und R^{10} jeweils unabhängig Wasserstoffatom, Halogenatom, $(C_1\text{-}C_4)$Alkylgruppe, Tri$(C_1\text{-}C_4)$alkylsilyloxy$(C_1\text{-}C_4)$alkylgruppe, Nitrogruppe, $(C_1\text{-}C_4)$Haloalkylgruppe, Hydroxy$(C_1\text{-}C_4)$alkylqruppe, Formylgruppe, $(C_1\text{-}C_4)$Alkoxygruppe, $(C_2\text{-}C_4)$Alkenyloxygrupe, $(C_2\text{-}C_4)$Alkinyloxygruppe, $(C_1\text{-}C_4)$Haloalkoxygruppe, $(C_1\text{-}C_4)$ Haloalkylthiogruppe, $(C_1\text{-}C_4)$Alkoxy$(C_1\text{-}C_4)$alkoxygruppe, $(C_1\text{-}C_4)$Alkoxygruppe mit einer Phenylgruppe, die gegebenenfalls durch ein Halogenatom substituiert ist, oder $(C_1\text{-}C_4)$Alkoxygruppe mit einer Phenoxygruppe, die gegebenenfalls durch CF_3, Halogenatom oder $(C_1\text{-}C_2)$Alkylgruppe substituiert ist, darstellen;

R^{11} ein Wasserstoffatom, Cyanogruppe, $(C_1\text{-}C_4)$Haloalkylthiogruppe, $(C_2\text{-}C_5)$Acylgruppe, Tri$(C_1\text{-}C_4)$alkylcarbomoylgruppe, $(C_1\text{-}C_4)$Alkoxycarbonylgruppe, $(C_1\text{-}C_4)$Alkoxycarbonylgruppe, $(C_2\text{-}C_4)$Alkenylgruppe oder $(C_1\text{-}C_4)$Alkylgruppe, die gegebenenfalls durch ein Halogenatom, $(C_1\text{-}C_4)$Alkoxygruppe, $(C_1\text{-}C_6)$Alkylcarbonyloxygruppe oder $(C_1\text{-}C_4)$Alkoxycarbonylgruppe substituiert ist, darstellt;

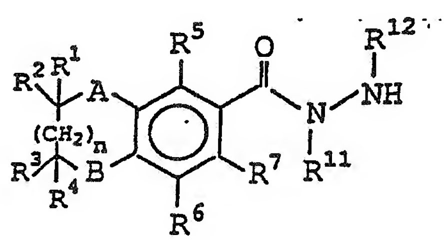
R^{12} eine verzweigte $(C_3\text{-}C_{10})$Alkylgruppe darstellt; und

n 0 oder 1 darstellt;

mit dem Vorbehalt, daß, wenn A und B jeweils unabhängig -O- oder

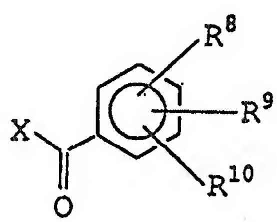


wobei R und R' jeweils unabhängig ein Wasserstoffatom oder $(C_1\text{-}C_4)$Alkylgruppe darstellen, mindestens einer von R^5, R^6 und R^7 kein Wasserstoffatom ist,
welches Umsetzung eines durch die Formel (II) dargestellten Hydrazids:



(II)

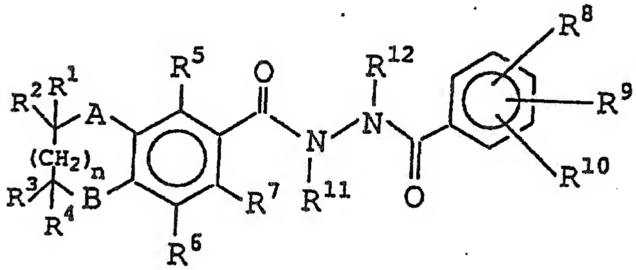
wobei R^1 bis R^7, R^{11}, R^{12}, A, B und n wie oben definiert sind,
mit einem durch die Formel (III) dargestellten Benzoylhalogenid:



; (III)

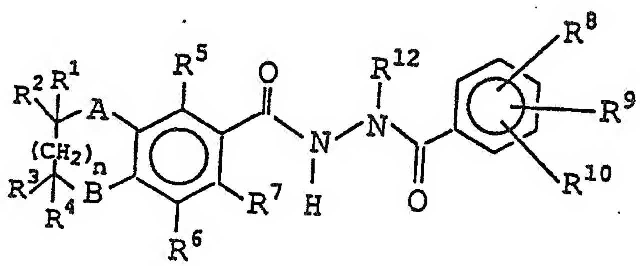
wobei X ein Halogenatom ist und R^8 bis R^{10} wie oben definiert sind,
in einem inerten Lösungsmittel in Gegenwart einer Base umfaßt.

2. Ein Verfahren zur Herstellung eines durch die Formel (I) dargestellten Hydrazinderivats:



(I)

wobei R^1 bis R^{10}, R^{12}, A, B und n wie in Anspruch 1 definiert sind und R^{11} eine Cyanogruppe, $(C_1\text{-}C_4)$Haloalkylthiogruppe, $(C_2\text{-}C_5)$Acylgruppe, Di$(C_1\text{-}C_4)$alkylcarbomoylgruppe, $(C_1\text{-}C_4)$Alkoxycarbonylgruppe, $(C_1\text{-}C_4)$Alkoxycarbonylcarbonylgruppe, $(C_1\text{-}C_4)$Alkylgruppe, die gegebenenfalls mit einem Halogenatom, $(C_1\text{-}C_4)$Alkoxygruppe, $(C_1\text{-}C_6)$Alkylcarbonyloxygruppe oder $(C_1\text{-}C_4)$Alkoxycarbonylgruppe substituiert ist, oder $(C_2\text{-}C_4)$Alkenylgruppe darstellt,
welches Reaktion eines durch die Formel (Ia) dargestellten Hydrazinderivats:



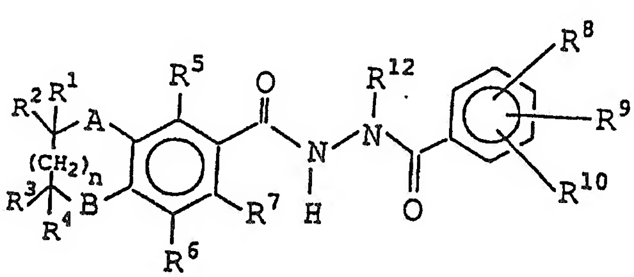
(Ia)

wobei R^1 bis R^{10}, R^{12}, A, B und n wie in Anspruch 1 definiert sind,
mit einem durch die Formel (IIa) dargestellten Halogenid:

$$X\text{-}R^{11} \qquad \text{(IIa)}$$

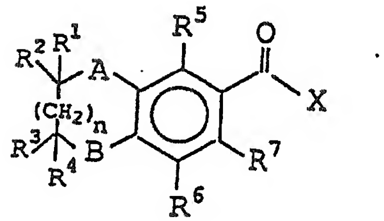
wobei X ein Halogenatom ist und R^{11} wie oben definiert ist,
in einem inerten Lösungsmittel in Gegenwart einer Base umfaßt.

3. Ein Verfahren zur Herstellung eines durch die Formel (Ia) dargestellten Hydrazinderivats:



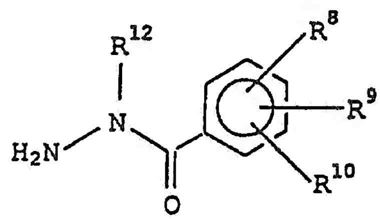
(Ia)

wobei R^1 bis R^{10}, R^{12}, A, B und n wie in Anspruch 1 definiert sind,
welches Umsetzung eines durch die Formel (IV) dargestellten Benzoylhalogenids:



(IV)

wobei R^1 bis R^7, A, B und n wie in Anspruch 1 definiert sind, und X ein Halogenatom ist, mit einem durch die Formel (IX) dargestellten Hydrazid:



(IX)

wobei R^8 bis R^{10} und R^{12} wie in Anspruch 1 definiert sind, in einem inerten Lösungsmittel in Gegenwart einer Base umfaßt.

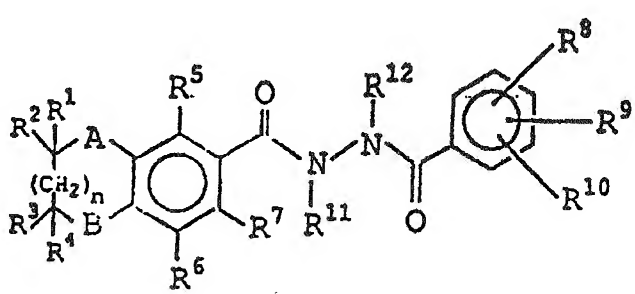
4. Modifikation des Verfahrens aus Ansprüchen 1 bis 3, zusätzlich umfassend Mischen oder Präsentation der entsprechend einem oder mehreren der Ansprüche 1 bis 3 erhaltenen Verbindung mit einem pestizidverträglichen Hilfsstoff und gegebenenfalls anderen pestizidwirksamen Substanzen und/oder Synergisten.

5. Pestizide Zusammensetzung, die 0,02 bis 95 Gew.-% einer entsprechend einem oder mehreren der Ansprüche 1 bis 3 erhaltenen Verbindung und einen pestizidverträglichen Hilfsstoff und, gegebenenfalls andere pestizidwirksame Substanzen und/oder Synergisten umfaßt.

Revendications

Revendications pour les Etats contractants suivants : AT, BE, CH, DE, DK, FR, GB, GR, IT, LI, LU, NL, SE

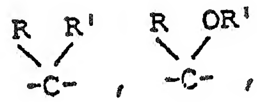
1. Dérivé d'hydrazine représenté par la formule suivante (I):

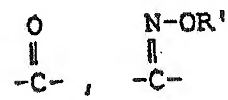


(I)

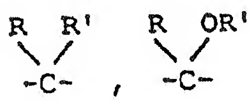
dans laquelle

A et B représentent chacun indépendamment -O-, -S-,





ou NR', où R représente un atome d'hydrogène, un groupe alkyle (C_1-C_4) ou un groupe alkoxy (C_1-C_4), R' représente un atome d'hydrogène, un groupe alkyle (C_1-C_4), un groupe acyle (C_2-C_4) ou un groupe p-fluorobenzyle, ou R et R' peuvent être combinés pour former un cycle dioxolanne avec l'atome de carbone auquel sont liés R et R', A ou B formant éventuellement une double liaison avec un atome de carbone adjacent lorsque A et B représentent chacun, de manière indépendante,



ou NR';

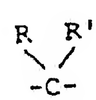
R^1, R^2, R^3 et R^4 représentent chacun, de manière indépendante un atome d'hydrogène, un groupe alkyle (C_1-C_4), un groupe alkoxy (C_1-C_4) alkyle (C_1-C_4), ou un groupe benzyloxyalkyle (C_1-C_4);

R^5, R^6 et R^7 représentent chacun, de manière indépendante, un atome d'hydrogène, un atome d'halogène, un groupe alkyle (C_1-C_4), un groupe nitro, un groupe amino, un groupe cyano, un groupe hydroxyle, un groupe formyle, un groupe halogénoalkyle (C_1-C_4), un groupe alcényle (C_2-C_4), un groupe alkoxy (C_1-C_4), un groupe alkoxy (C_1-C_4)-alkyle (C_1-C_4), un groupe alkyle (C_1-C_4) thio alkyle (C_1-C_4) ou un groupe alkoxy-(C_1-C_4) alkoxy (C_1-C_4);

R^8, R^9 et R^{10} représentent chacun, de manière indépendante un atome d'hydrogène, un atome d'halogène un groupe alkyle (C_1-C_4), un groupe trialkyl(C_1-C_4)silyloxyalkyle (C_1-C4), un groupe nitro, un groupe halogénoalkyle (C_1-C_4), un groupe hydroxyalkyle (C_1-C_4), un groupe formyle, un groupe alkoxy (C_1-C_4), un groupe alcényloxy (C_2-C_4), un groupe alcynyloxy (C_2-C_4), un groupe alkényle (C_2-C_4), un groupe alcynyle (C_2-C_4), un groupe halogénoalkoxy (C_1-C_4), un groupe [halogénoalkyle(C_1-C_4)thio], un groupe alkoxy (C_1-C_4) alkoxy (C_1-C_4); un groupe alkoxy (C_1-C_4) possédant un groupe phényle qui est éventuellement substitué par un atome d'halogène, ou un groupe alkoxy (C_1-C_4) possédant un groupe phénoxy qui est éventuellement substitué par un groupe CF_3, un atome d'halogène ou un groupe alkyle (C_1-C_2);

R^{11} représente un atome d'hydrogène, un groupe cyano, un groupe [halogénoalkyle(C_1-C_4)thio], un groupe acyle (C_2-C_5), un groupe dialkyl(C_1-C_4) carbamoyle, un groupe alkoxy (C_1-C_4) carbonyle, un groupe alkoxy (C_1-C_4) carbonylcarbonyle, un groupe alcényle (C_2-C_4) ou un groupe alkyle (C_1-C_4), qui est éventuellement substitué par un atome d'halogène, un groupe alkoxy (C_1-C_4), un groupe alkyl (C_1-C_6) carbonyloxy ou un groupe alkoxy (C_1-C_4) carbonyle;

R^{12} représente un groupe alkyle (C_3-C_{10}) ramifié et n représente 0 ou 1; sous réserve que, lorsque A et B représentent chacun de manière indépendante -O- ou



où R et R' représentent chacun de manière indépendante un atome d'hydrogène ou un groupe alkyle (C_1-C_4), au moins l'un des groupes R^5, R^6 et R^7 n'est pas un atome d'hydrogène.

2. Dérivé d'hydrazine selon la revendication 1, où:

A représente -O- ou -CH_2-;

B représente -O- ou -CH_2-;

R^1, R^2, R^2 et R^4 représentent chacun, de manière indépendante, un atome d'hydrogène ou un groupe méthyle;

R^5 représente un groupe alkyle (C_1-C_4), un groupe halogénoalkyle (C_1-C_4) ou un atome d'halogène;

R^6 représente un atome d'hydrogène, un groupe alkyle (C_1-C_4) ou un atome d'halogène;

R^7 représente un atome d'hydrogène ou un atome d'halogène;

R^8, R^9 et R^{10} représentent chacun, de manière indépendante, un atome d'hydrogène, un groupe alkyle(C_1-C_4), un groupe halogénoalkyle (C_1-C_4), un atome d'halogène, un groupe nitro, un groupe alkoxy (C_1-C_4), un groupe alcényloxy (C_2-C_4), un groupe alcynyloxy (C_2-C_4), un groupe alcényle (C_2-C_4), un groupe halogénoalkoxy (C_1-C_4), un groupe phénylalkoxy (C_1-C_4), dont le résidu phényle est éventuellement substitué avec un atome d'halogène, ou un groupe phénoxyalkoxy (C_1-C_4) dont le résidu phényle est éventuellement substitué avec un groupe alkyle (C_1-C_2), un groupe CF_3 ou un atome d'halogène;

R^{11} représente un atome d'hydrogène, un groupe cyano, un groupe [halogénoalkyle(C_1-C_4)thio], un groupe alkoxy (C_1-C_4) carbonylcarbonyle ou un groupe alkyl (C_1-C_4) carbonyloxyméthyle;

R^{12} représente un groupe alkyle ramifié (C_4-C_8) et n représente 0;

3. Dérivé d'hydrazine selon la revendication 1, où:

A représente -O- ou -CH_2-;

B représente -O-;

R^1, R^2, R3^2 et R^4 représentent chacun un atome d'hydrogène;

R^5 représente un groupe alkyle (C_1-C_2), un groupe halogénoalkyle (C_1-C_2) ou un atome d'halogène;

R^6 représente un atome d'hydrogène;

R^7 représente un atome d'hydrogène;

R^8, R^9 et R^{10} représentent chacun, de manière indépendante, un atome d'hydrogène, un groupe alkyle(C_1-C_2), un groupe halogénoalkyle (C_1-C_2), un atome d'halogène, un groupe nitro ou un groupe alkoxy (C_1-C_2);

R^{11} représente un atome d'hydrogène, un groupe cyano, un groupe trichlorométhylthio, un groupe éthoxycarbonylcarbonyle ou un groupe pivaloyloxyméthyle;

R^{12} représente un groupe alkyle (C_4-C_6) ramifié et n représente 0.

4. Dérivé d'hydrazine selon la revendication 1, où:

A représente -O- ou -CH_2-;

B représente -O-;

R^1, R^2, R^3 et R^4 représentent chacun un atome d'hydrogène;

R^5 représente un groupe alkyle (C_1-C_2);

R^6 représente un atome d'hydrogène;

R^7 représente un atome d'hydrogène;

R^8, R^9 et R^{10} représentent chacun, de manière indépendante, un atome d'hydrogène, un groupe méthyle, un groupe mono-, di-, ou trifluorométhyle, un atome de chlore, un atome de fluor, un groupe nitro ou un groupe méthoxy;

R^{11} représente un atome d'hydrogène, un groupe cyano, un groupe trichlorométhylthio, un groupe éthoxycarbonylcarbonyle ou un groupe pivaloyloxyméthyle;

R^{12} représente un groupe alkyle ramifié (C_4-C_6) et n représente 0.

5. Dérivé d'hydrazine selon la revendication 1, où:

A représente -O- ou -CH_2-;

B représente -O-;

R^1, R^2, R^3 et R^4 représentent chacun un atome d'hydrogène;

R^5 représente un groupe alkyle (C_1-C_2);

R^6 représente un atome d'hydrogène;

R^7 représente un atome d'hydrogène;

R^8, R^9 et R^{10} représentent, ensemble, avec le groupe phényle auquel ils sont liés, un groupe 3,5-diméthylphényle, un groupe 3,5-dichlorophényle, un groupe 2,4-dichlorophényle, un groupe 3-fluorométhyl-5-méthylphényle, un groupe 3-difluorométhyl-5-méthylphényle ou un groupe 3,5-diméthyl-4-fluorophényle;.

R^{11} représente un atome d'hydrogène, un groupe cyano ou un groupe trichlorométhylthio;

R^{12} représente un groupe t-butyle, un groupe 2,2-diméthylpropyle ou un groupe 1,2,2-triméthylpropyle et

n représente 0.

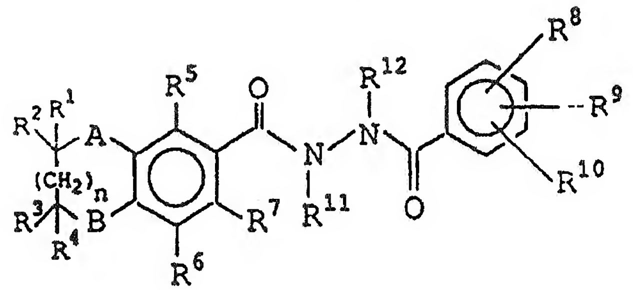
6. Dérivé d'hydrazine selon la revendication 1, choisi au sein du groupe constitué par :

N-(5-méthylchroman-6-carbo)-N'-t-butyl-N'-(3,5-diméthylbenzoyl)hydrazine,
N-cyano-N-(5-méthylchroman-6-carbo)-N'-t-butyl-N'-(3,5-diméthylbenzoyl)hydrazine,
N-(5-méthylchroman-6-carbo)-N'-t-butyl-N'-(3,5-diméthyl-4-fluorobenzoyl)hydrazine,
N-(5-méthylchroman-6-carbo) -N-trichlorométhylthio-N'-t-butyl-N'-(3,5-diméthylbenzoyl)hydrazine,
N-(5-méthyl-1,4-benzodioxan-6-carbo)-N'-(2,2-diméthylpropyl)-N'-(3,5-diméthylbenzoyl)hydrazine,
N-cyano-N-(5-méthyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-diméthylbenzoyl)hydrazine,
N-(5-méthyl-1,4-benzodioxan-6-carbo)-N-trichlorométhylthio-N'-t-butyl-N'-(3,5-diméthylbenzoyl)hydrazine,
N-(5-méthyl-1,4benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-dichlorobenzoyl)hydrazine,
N-(5-méthyl-1,4-bendioxan-6-carbo)-N'-t-butyl-N'-(3-difluorométhyl-5-méthylbenzoyl)hydrazine,
N-(5-méthyl-1,4benzodioxan-6-carbo)-N'-(1,2,2-triméthylpropyl)-N'-(3,5-diméthylbenzoyl)hydrazine, et
N-(5-méthyl-1,4-benzodioxan-6-carbo)-N'-t-butyl-N'-(3,5-diméthylbenzoyl)hydrazine.

7. Composition pesticide qui comprend une quantité efficace en tant que pesticide d'un dérivé d'hydrazine selon l'une quelconque des revendications 1 à 6 en tant que principe actif et un adjuvant acceptable sur le plan pesticide.

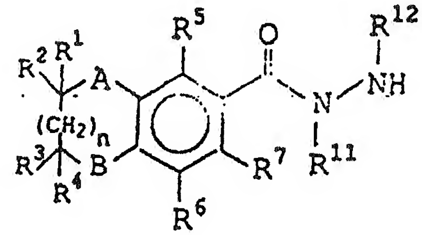
8. Procédé de lutte contre une espèce nuisible qui comprend l'application de dérivé d'hydrazine selon l'une quelconque des revendications 1 à 6 sur l'espèce nuisible.

9. Procédé de production d'un dérivé d'hydrazine de formule (I):



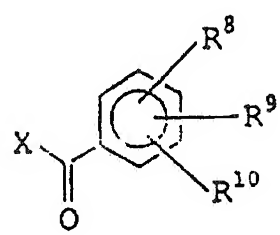
(I)

dans laquelle les résidus R^1 à R^{12}, A, B et n sont tels que définis à la revendication 1, qui comprend la mise en réaction d'une hydrazine de formule (II):



(II)

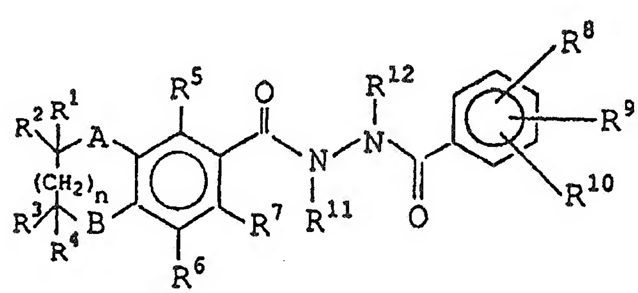
dans laquelle les résidus R^1 à R^7, R^{11}, R^{12}, A, B et n sont tels que définis à la revendication 1, avec un halogénure de benzoyle de formule (III):



(III)

où X est un atome d'halogène et R^8 à R^{10} sont tels que définis à la revendication 1, dans un solvant inerte en présence d'une base.

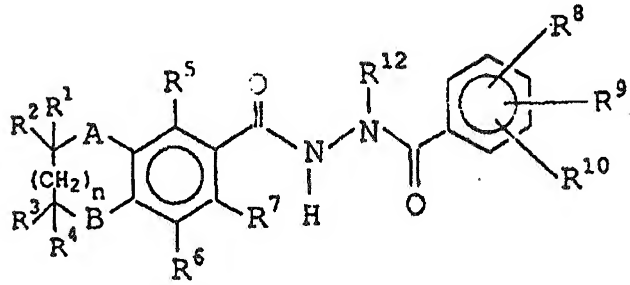
10. Procédé de production d'un dérivé d'hydrazine de formule (I):



(I)

dans laquelle les résidus R^1 à R^{10}, R^{12}, A, B et n sont tels que définis à la revendication 1, et R^{11} est un groupe cyano, un groupe [halogénoalkyle (C_1-C_4)thio], un groupe acyle (C_2-C_5), un groupe dialkyl (C_1-C_4) carbamoyle,

un groupe alkoxy (C_1-C_4) carbonyle, un groupe alkoxy (C_1-C_4) carbonylcarbonyle, un groupe alkyle (C_1-C_4) qui est éventuellement substitué par un atome d'halogène, un groupe alkoxy (C_1-C_4), un groupe alkyl (C_1-C_6) carbonyloxy, un groupe alkoxy (C_1-C_4) carbonyle ou un groupe alkényle (C_2-C_4),
qui comprend la mise en réaction d'un dérivé d'hydrazine de formule (Ia):



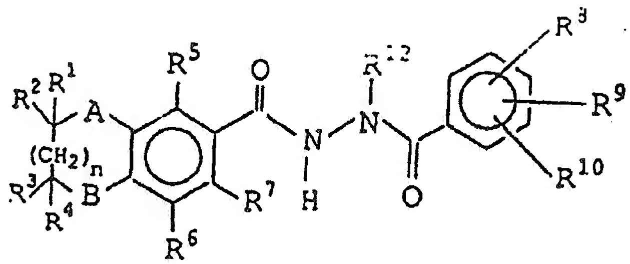
(Ia)

dans laquelle les résidus R^1 à R^{10}, R^{12}, A, B et n sont tels que définis à la revendication 1, avec un halogénure de formule (IIa):

$$X\text{-}R^{11} \qquad \text{(IIa)}$$

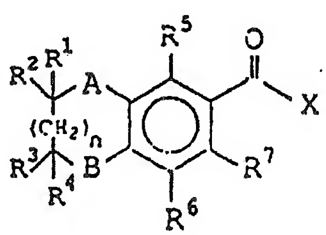
où X est un atome d'halogène et R^1 est tel que définis ci-dessus, dans un solvant inerte en présence d'une base.

11. Procédé de production d'un dérivé d'hydrazine de formule (Ia):



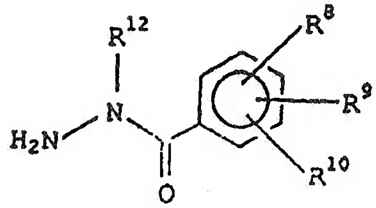
(Ia)

dans laquelle les résidus R^1 à R^{10}, R^{12}, A, B et n sont tels que définis à la revendication 1, qui comprend la mise en réaction d'un halogénure de benzoyle de formule (IV):



(IV)

dans laquelle les résidus R^1 à R^7, A, B et n sont tels que définis à la revendication 1, et X est un atome d'halogène avec une hydrazine de formule (IX):

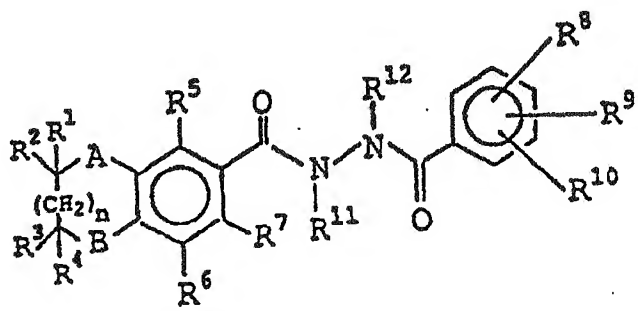


(IX)

où R^8 à R^{10} et R^{12} sont tels que définis à la revendication 1, dans un solvant inerte en présence d'une base.

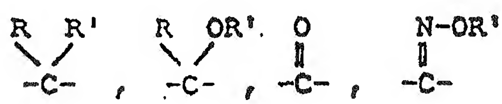
Revendications pour l'Etat contractant suivant : ES

1. Procédé de production d'un dérivé d'hydrazine représenté par la formule suivante (I):



(I)

dans laquelle A et B représentent chacun indépendamment -O-, -S-,



ou NR', où R représente un atome d'hydrogène, un groupe alkyle (C_1-C_4) ou un groupe alkoxy (C_1-C_4), R' représente un atome d'hydrogène, un groupe alkyle (C_1-C_4), un groupe acyle (C_2-C_4) ou un groupe p-fluorobenzyle, ou R et R' peuvent être combinés pour former un cycle dioxolanne avec l'atome de carbone auquel sont liés R et R', A ou B formant éventuellement une double liaison avec un atome de carbone adjacent lorsque A et B représentent chacun, de manière indépendante,

ou NR';

R^1, R^2, R^3 et R^4 représentent chacun, de manière indépendante un atome d'hydrogène, un groupe alkyle (C_1-C_4), un groupe alkoxy (C_1-C_4) alkyle (C_1-C_4), ou un groupe benzyloxyalkyle (C_1-C_4);

R^5, R^6 et R^7 représentent chacun, de manière indépendante, un atome d'hydrogène, un atome d'halogène, un groupe alkyle (C_1-C_4), un groupe nitro, un groupe amino, un groupe cyano, un groupe hydroxyle, un groupe formyle, un groupe halogénoalkyle (C_1-C_4), un groupe alcényle (C_2-C_4), un groupe alkoxy (C_1-C_4), un groupe

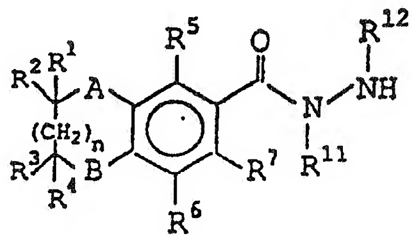
alkoxy (C_1-C_4)-alkyle (C_1-C_4), un groupe alkyle (C_1-C_4) thio alkyle (C_1-C_4) ou un groupe alkoxy-(C_1-C_4) alkoxy (C_1-C_4);

R^8, R^9 et R^{10} représentent chacun, de manière indépendante un atome d'hydrogène, un atome d'halogène un groupe alkyle (C_1-C_4), un groupe trialkyl(C_1-C_4)silyloxyalkyle (C_1-C_4), un groupe nitro, un groupe halogénoalkyle (C_1-C_4), un groupe hydroxyalkyle (C_1-C_4), un groupe formyle, un groupe alkoxy (C_1-C_4), un groupe alcényloxy (C_2-C_4), un groupe alcynyloxy (C_2-C_4), un groupe alkényle (C_2-C_4), un groupe alcynyle (C_2-C_4), un groupe halogénoalkoxy (C_1-C_4), un groupe [halogénoalkyle(C_1-C_4)thio], un groupe alkoxy (C_1-C_4) alkoxy (C_1-C_4); un groupe alkoxy (C_1-C_4) possédant un groupe phényle qui est éventuellement substitué par un atome d'halogène, ou un groupe alkoxy (C_1-C_4) possédant un groupe phénoxy qui est éventuellement substitué par un groupe CF_3, un atome d'halogène ou un groupe alkyle (C_1-C_2);

R^{11} représente un atome d'hydrogène, un groupe cyano, un groupe [hagénoalkyle(C_1-C_4)thio], un groupe acyle (C_2-C_5), un groupe dialkyl(C_1-C_4) carbamoyle, un groupe alkoxy (C_1-C_4) carbonyle, un groupe alkoxy (C_1-C_4) carbonylcarbonyle, un groupe alcényle (C_2-C_4) ou un groupe alkyle (C_1-C_4), qui est éventuellement substitué par un atome d'halogène, un groupe alkoxy (C_1-C_4), un groupe alkyl (C_1-C_6) carbonyloxy ou un groupe alkoxy (C_1-C_4) carbonyle;

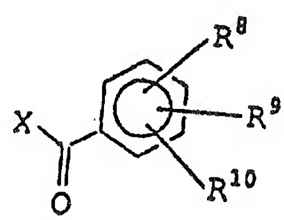
R^{12} représente un groupe alkyle(C_3-C_{10}) ramifié et n représente 0 ou 1;

sous réserve que, lorsque A et B représentent chacun de manière indépendante -O- ou où R et R' représentent chacun de manière indépendante un atome d'hydrogène ou un groupe alkyle (C_1-C_4), au moins l'un des groupes R^5, R^6 et R^7 n'est pas un atome d'hydrogène, qui comprend la mise en réaction d'une hydrazine de formule (II):



(II)

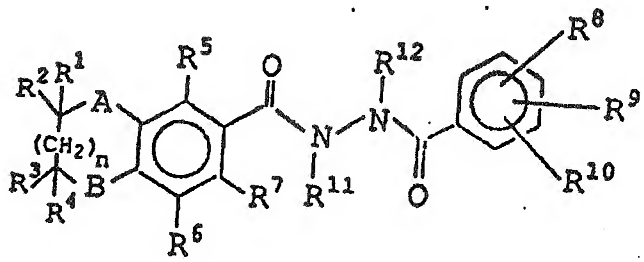
dans laquelle les résidus R^1 à R^7, R^{11}, R^{12}, A , B et n sont tels que définis ci-dessus, avec un halogénure de benzoyle formule (III):



; (III)

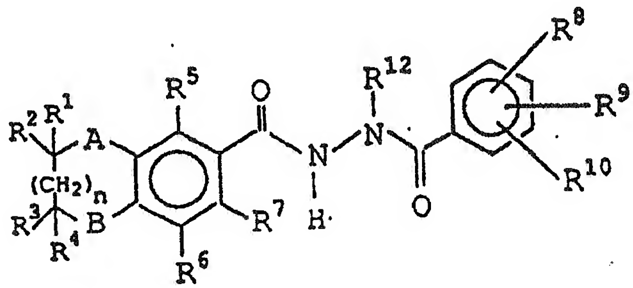
où X est un atome d'halogène et R^8 à R^{10} sont tels que défini ci-dessus, dans un solvant inerte en présence d'une base.

2. Procédé de production d'un dérivé d'hydrazine de formule (I):



(I)

dans laquelle les résidus R^1 à R^{10}, R^{12}, A, B et n sont tels que définis à la revendication 1, et R^{11} est un groupe cyano, un groupe [halogénoalkyle(C_1-C_4)thio], un groupe acyle (C_2-C_5), un groupe dialkyl (C_1-C_4) carbamoyle, un groupe alkoxy (C_1-C_4) carbonyle, un groupe alkoxy (C_1-C_4) carbonylcarbonyle, un groupe alkyle (C_1-C_4) qui est éventuellement substitué par un atome d'halogène, un groupe alkoxy (C_1-C_4), un groupe alkyl (C_1-C_6) carbonyloxy, un groupe alkoxy (C_1-C_4) carbonyle ou un groupe alcényle (C_2-C_4),
qui comprend la mise en réaction d'un dérivé d'hydrazine de formule (Ia):



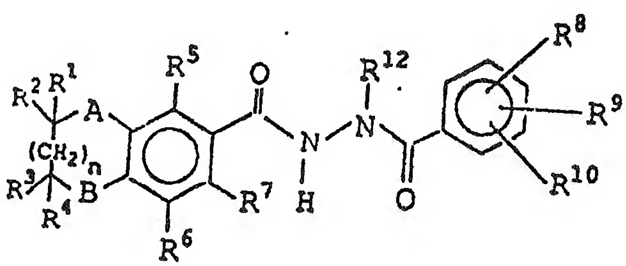
(Ia)

dans laquelle les résidus R^1 à R^{10}, R^{12}, A, B et n sont tels que définis à la revendication 1, avec un halogénure de formule (IIa):

$$X\text{-}R^{11} \qquad \text{(IIa)}$$

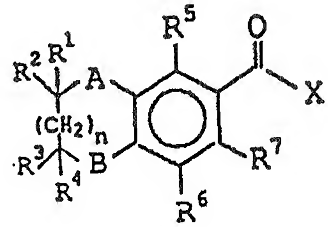
où X est un atome d'halogène et R^{11} est tel que défini ci-dessus, dans un solvant inerte en présence d'une base.

3. Procédé de production d'un dérivé d'hydrazine de formule (Ia):



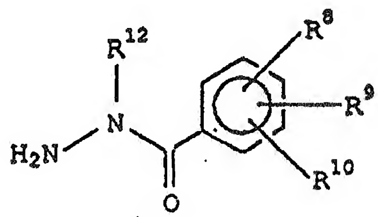
(Ia)

dans laquelle les résidus R^1 à R^{10}, R^{12}, A, B et n sont tels que définis à la revendication 1, qui comprend la mise en réaction d'un halogénure de benzoyle de formule (IV):



(IV)

dans laquelle les résidus R^1 à R^7, A, B et n sont tels que définis à la revendication 1, et X est un atome d'halogène avec une hydrazine de formule (IX):



(IX)

ou R^8 à R^{10} et R^{12} sont tels que définis à la revendication 1, dans un solvant inerte en présence d'une base.

4. Modification du procédé selon les revendications 1 à 3, comprenant en outre le mélange du composé obtenu conformément à l'une, au moins, des revendications 1 à 3, ou la présentation de ce produit, avec un adjuvant acceptable sur le plan pesticide et éventuellement avec d'autres substances actives et/ou synergiques sur le plan pesticide.

5. Composition pesticide qui comprend de 0,02 à 95% en poids d'un composé obtenu conformément à l'une, au moins, des revendications 1 à 3, et un adjuvant acceptable sur le plan pesticide et éventuellement d'autres substances actives et/ou synergiques sur le plan pesticide.